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**For: PROCESS FOR PREPARING MICROENCAPSULATED PIGMENT,  
MICROENCAPSULATED PIGMENT, AQUEOUS DISPERSION, AND INK FOR  
INK JET RECORDING**

Commissioner for Patents  
Alexandria, V.A. 22313-1450

**STATEMENT UNDER 37 C.F.R. 1.55**

Sir,

I, Katsuya TAKENAKA, hereby declare that I am conversant with both English and Japanese languages, and certify to best of my knowledge and belief that the attached is a true and correct English translation of Japanese Patent Application No. 2003-307852 filed in the Japanese Patent and Trademark Office on August 29, 2003 in the Japanese language.

**Katsuya TAKENAKA**

**Date: March 19, 2007**

[Designation of Document] CLAIMS

[Claim 1] An ink for ink jet recording containing an aqueous dispersion of a microencapsulated pigment which is formed by adding (c) an anionic polymerizable surfactant and/or a hydrophilic monomer having an anionic group to an aqueous dispersion in which pigment particles are dispersed and polymerizing the added aqueous dispersion, the ink for ink jet recording being prepared by purifying the aqueous dispersion of the microencapsulated pigment,

wherein the concentration of unreacted (c) after the purification treatment is 50000 ppm or less based on the aqueous component in the aqueous dispersion.

[Claim 2] The ink for ink jet recording according to claim 1, wherein the ink is obtained by adding (b) a hydrophobic monomer to the aqueous dispersion in which the pigment particles are dispersed and conducting emulsion polymerization, and the total concentration of the unreacted (b) and (c) after the purification treatment is 50000ppm or less based on aqueous components in the aqueous dispersion.

[Claim 3] The ink for ink jet recording according to claim 1 or 2, wherein the pigment particles have a hydrophilic group on the surfaces thereof.

[Claim 4] An ink for ink jet recording containing an aqueous dispersion of a microencapsulated pigment which is

formed by adding (a) a cationic polymerizable surfactant and (c) an anionic polymerizable surfactant and/or a hydrophilic monomer having an anionic group to an aqueous dispersion in which pigment particles having an anionic group on the surface thereof are dispersed and polymerizing the added aqueous dispersion, the ink for ink jet recording being prepared by purifying the aqueous dispersion of the microencapsulated pigment,

wherein the total concentration of unreacted (a) and (c) after the purification treatment is 50000 ppm or less based on the aqueous component in the aqueous dispersion.

[Claim 5] The ink for ink jet recording according to claim 4, wherein the ink is obtained by adding (b) a hydrophobic monomer to the aqueous dispersion in which the pigment particles having the anionic group on the surfaces thereof are dispersed and conducting emulsion polymerization, and the total concentration of the unreacted (a), (b), and (c) after the purification treatment is 50000ppm or less based on aqueous components in the aqueous dispersion.

[Claim 6] The ink for ink jet recording according to claim 5, wherein the concentrations of the unreacted (a), (b), and (c) before the purification treatment are in the range of 5 to 40% by weight based on the added amounts, respectively.

[Designation of Document] SPECIFICATION

[Title of the Invention] INK FOR INK JET RECORDING

[Technical Field]

[0001]

The present invention relates to an ink for ink jet recording containing a microencapsulated pigment.

[Background Art]

[0002]

An ink jet recording process is a process comprising ejecting ink droplets from a fine nozzle head to form letters or figures on a surface of a recording medium such as paper. As the ink jet recording process, there has been put to practical use a process in which electric signals are converted to mechanical signals with an electrostrictive element, thereby intermittently ejecting ink droplets stored in a nozzle head section to record letters or symbols on a surface of a recording medium, a process in which a part of an ink solution is rapidly heated at a portion close to an ejection portion of a nozzle head to generate bubbles, and ink droplets are intermittently ejected by volume expansion due to the bubbles to record letters or symbols on a surface of a recording medium, or the like.

[0003]



As an ink for ink jet recording, there has recently been provided an aqueous pigment ink in which a pigment is dispersed in water. This is because an ink using a pigment is characterized by excellent water resistance and light resistance, compared to an ink using a water-soluble dye. In such an aqueous pigment ink, it has been generally carried out that the pigment is dispersed in an aqueous dispersing medium with a dispersant such as a surfactant or a polymer dispersant.

For example, in Patent Document 1, in a pigment ink using an acetylene glycol-based penetrant, it has been studied to use a polymer dispersant as the dispersant for pigment particles, and water, a non-volatile organic solvent or a lower alcohol as the aqueous medium, thereby securing dispersion stability thereof. However, when the dispersant is used for dispersion of the pigment particles as described above, elements in ink preparation are increased, which makes it difficult to set ink physical properties such as viscosity to desired values. Further, also in this pigment ink, the problem that print density is difficult to be secured is not solved yet.

Furthermore, in the aqueous pigment ink, the dispersant is merely adsorbed on surfaces of the pigment particles. Accordingly, when the ink solution is ejected through fine nozzles of a recording head, strong shear

force is applied thereto, so that the dispersant adsorbed on the surfaces of the pigment particles is eliminated to deteriorate dispersibility, resulting in recognition of the tendency of ejection to become unstable in some cases. Moreover, when the above-mentioned aqueous pigment ink is stored for a long period of time, the tendency of ejection to become unstable is also recognized in some cases.

[0004]

As another technique for dispersing pigment particles in water, there has been proposed a technique of introducing a sulfonic acid group onto a surface of the pigment particle. For example, in Patent Document 2, a pigment ink is described which contains a surface-sulfonated organic pigment obtained by treating with a sulfonating agent an organic pigment dispersed in an active proton-free solvent (related art 1). According to related art 1, it has been said that the above-mentioned pigment ink has excellent dispersion stability, and good ejection stability from the nozzles of the recording head (the characteristic of being stably ejected from the recording head to a definite direction).

For example, in Patent Document 3, it is described that an organic pigment mass whose surface is positively chargeable is prepared by treating a sulfonic acid group-introduced organic pigment mass with a monovalent metallic

ion. Furthermore, there have been known an aqueous ink composition excellent in storage stability (dispersion stability) containing fine pigment particles prepared from the organic pigment mass whose surface is positively chargeable, a dispersant and water (related art 2).

[0005]

However, although an ink using the surface-treated pigment particles of the above-mentioned related art 1 or related art 2 as a colorant is excellent in dispersion stability and ejection stability, compared to conventional pigment-based inks for ink jet recording, abrasion resistance of recorded matter obtained by printing on a recording medium such as plain paper or a recording medium for ink jet recording (a recording medium having provided on a surface thereof an ink receiving layer for receiving an ink for ink jet recording) has still been insufficient. This is considered to be due to insufficient fixability of the above-mentioned surface-treated pigment particles to the recording medium.

[0006]

On the other hand, in order to improve fixability of a pigment contained in a pigment-based ink jet recording ink to a recording medium, a technique using a microencapsulated pigment in which colorant particles are encapsulated with a polymer has been known.

Encapsulated fine pigment particles are known in patent documents 4 and 5, and pigment particles in which a polymer is graft polymerized on surfaces thereof are known in patent documents 6 to 9. Patent document 10 proposes a method for microencapsulating a hydrophobic powder with an amphiphilic graft polymer. However, the use of a previously polymerized polymer in microencapsulating has raised the problem that the particle size after encapsulation becomes too large.

In addition to the above-mentioned suggestions, Patent Documents 11 to 19 propose inks containing pigments encapsulated with resins having film forming properties at room temperature by phase reversal of emulsion, and patent documents 20 to 30 propose inks using pigments encapsulated with anionic group-containing organic polymer compounds by acid precipitation.

[0007]

Further, patent documents 31 to 35 propose inks using polymer emulsions in which fine polymer particles are impregnated with colorants by phase reversal of emulsion (related art 3). However, in the colorant obtained by phase reversal of emulsion or acid precipitation, the polymer adsorbed on the pigment particles is also sometimes eliminated and dissolved in the ink, depending on the kind of organic solvent such as

a penetrant used in the ink, so that dispersion stability and ejection stability of the ink, image quality and the like have been insufficient in some cases. In the ink of related art 3, the polymer adsorbed on the pigment particles is not a little eliminated, so that the pigment content in the ink is limited from the point of dispersion stability.

[0008]

Further, in patent document 36, a technique is known in which a polymerizable surfactant and an aqueous medium are added to pigment particles to prepare an emulsion of the pigment particles, and the polymerizable surfactant is polymerized to microencapsulate the pigment particles (related art 4). However, also in this case, dispersion stability and ejection stability of the ink, image quality and the like are still insufficient, so that the pigment content in the ink is limited from the point of dispersion stability.

[0009]

From the above, by using the inks in which the microencapsulated pigments of related art 3 and related art 4, print density of the obtained recorded images may be low. In particular, when plain paper is used as the recording medium, there have been problems that blurring is liable to occur in the images and that high color

developability is hardly obtained. In addition, when glossy paper is used as the recording medium, it is difficult to obtain a high glossy property.

[0010]

[Patent Document 1] Japanese Unexamined Patent Application Publication No. 3-157464

[Patent Document 2] Japanese Unexamined Patent Application Publication No. 10-110129

[Patent Document 3] Japanese Unexamined Patent Application Publication No. 11-49974

[Patent Document 4] Japanese Examined Patent Application Publication No. 7-94634 B

[Patent Document 5] Japanese Unexamined Patent Application Publication No. 8-59715

[Patent Document 6] Japanese Unexamined Patent Application Publication No. 5-339516

[Patent Document 7] Japanese Unexamined Patent Application Publication No. 8-302227

[Patent Document 8] Japanese Unexamined Patent Application Publication No. 8-302228

[Patent Document 9] Japanese Unexamined Patent Application Publication No. 8-81647

[Patent Document 10] Japanese Unexamined Patent Application Publication No. 5-320276

[Patent Document 11] Japanese Unexamined Patent  
Application Publication No. 8-218015

[Patent Document 12] Japanese Unexamined Patent  
Application Publication No. 8-295837

[Patent Document 13] Japanese Unexamined Patent  
Application Publication No. 9-3376

[Patent Document 14] Japanese Unexamined Patent  
Application Publication No. 8-183920

[Patent Document 15] Japanese Unexamined Patent  
Application Publication No. 10-46075

[Patent Document 16] Japanese Unexamined Patent  
Application Publication No. 10-292143

[Patent Document 17] Japanese Unexamined Patent  
Application Publication No. 11-80633

[Patent Document 18] Japanese Unexamined Patent  
Application Publication No. 11-349870

[Patent Document 19] Japanese Unexamined Patent  
Application Publication No. 2000-7961

[Patent Document 20] Japanese Unexamined Patent  
Application Publication No. 9-31360

[Patent Document 21] Japanese Unexamined Patent  
Application Publication No. 9-217019

[Patent Document 22] Japanese Unexamined Patent  
Application Publication No. 9-316353

[Patent Document 23] Japanese Unexamined Patent  
Application Publication No. 9-104834

[Patent Document 24] Japanese Unexamined Patent  
Application Publication No. 9-151342

[Patent Document 25] Japanese Unexamined Patent  
Application Publication No. 10-140065

[Patent Document 26] Japanese Unexamined Patent  
Application Publication No. 11-152424

[Patent Document 27] Japanese Unexamined Patent  
Application Publication No. 11-166145

[Patent Document 28] Japanese Unexamined Patent  
Application Publication No. 11-166145

[Patent Document 29] Japanese Unexamined Patent  
Application Publication No. 11-199783

[Patent Document 30] Japanese Unexamined Patent  
Application Publication No. 11-209672

[Patent Document 31] Japanese Unexamined Patent  
Application Publication No. 9-286939

[Patent Document 32] Japanese Unexamined Patent  
Application Publication No. 2000-44852

[Patent Document 33] Japanese Unexamined Patent  
Application Publication No. 2000-53897

[Patent Document 34] Japanese Unexamined Patent  
Application Publication No. 2000-53898



[Patent Document 35] Japanese Unexamined Patent  
Application Publication No. 2000-53899

[Patent Document 36] Japanese Unexamined Patent  
Application Publication No. 10-316909

[Disclosure of the Invention]

[Problems that the Invention is to Solve]

[0011]

The present invention has been made in view of the above-mentioned problems. An object of the invention is to provide an ink for ink jet recording in which a print density of a recorded image is high, blurring hardly occurs when plain paper is used as a recording medium, and a glossy property is excellent when glossy paper is used.

[Means for Solving the Problems]

[0012]

The technical configurations of the invention are as follows.

1. An ink for ink jet recording containing an aqueous dispersion of a microencapsulated pigment which is formed by adding (c) an anionic polymerizable surfactant and/or a hydrophilic monomer having an anionic group to an aqueous dispersion in which pigment particles are dispersed and polymerizing the added aqueous dispersion, the ink for ink jet recording being prepared by purifying the aqueous dispersion of the microencapsulated pigment,

wherein the concentration of unreacted (c) after the purification treatment is 50000 ppm or less based on the aqueous component in the aqueous dispersion.

[0013]

2. The ink for ink jet recording according to 1., wherein the ink is obtained by adding (b) a hydrophobic monomer to the aqueous dispersion in which the pigment particles are dispersed and conducting emulsion polymerization, and the total concentration of the unreacted (b) and (c) after the purification treatment is 50000ppm or less based on aqueous components in the aqueous dispersion.

3. The ink for ink jet recording according to 1. or 2., wherein the pigment particles have a hydrophilic group on the surfaces thereof.

[0014]

4. An ink for ink jet recording containing an aqueous dispersion of a microencapsulated pigment which is formed by adding (a) a cationic polymerizable surfactant and (c) an anionic polymerizable surfactant and/or a hydrophilic monomer having an anionic group to an aqueous dispersion in which pigment particles having an anionic group on the surface thereof are dispersed and polymerizing the added aqueous dispersion, the ink for ink

jet recording being prepared by purifying the aqueous dispersion of the microencapsulated pigment,

wherein the total concentration of unreacted (a) and (c) after the purification treatment is 50000 ppm or less based on the aqueous component in the aqueous dispersion.

[0015]

5. The ink for ink jet recording according to 4., wherein the ink is obtained by adding (b) a hydrophobic monomer to the aqueous dispersion in which the pigment particles having the anionic group on the surfaces thereof are dispersed and conducting emulsion polymerization, and the total concentration of the unreacted (a), (b), and (c) after the purification treatment is 50000ppm or less based on aqueous components in the aqueous dispersion.

6. The ink for ink jet recording according to 5., wherein the concentrations of the unreacted (a), (b), and (c) before the purification treatment are in the range of 5 to 40% by weight based on the added amounts, respectively.

[Advantages of the Invention]

[0016]

According to the ink for ink jet recording of the invention, by setting the concentration of the unreacted (c) to 50000 ppm or less by means of the purification treatment, it is possible to obtain an ink for ink jet

recording in which a print density of a recorded image is high, blurring hardly occurs when plain paper is used as a recording medium, and a glossy property is excellent when glossy paper is used.

[Mode for Carrying out the Invention]

[0017].

A microencapsulated pigment according to the invention includes pigment particles encapsulated with a polymer and can be obtained by adding (c) an anionic polymerizable surfactant and/or a hydrophilic monomer having an anionic group to an aqueous dispersion in which pigment particles are dispersed and polymerizing the added aqueous dispersion, the ink for ink jet recording being prepared by purifying the aqueous dispersion of the microencapsulated pigment.

The microencapsulated pigment can be suitably prepared by preparing an aqueous dispersion in advance in which pigment particles are dispersed in an aqueous medium, adding an anionic polymerizable surfactant and/or a hydrophilic monomer having an anionic group to the aqueous dispersion and performing an emulsion process thereto, and adding a polymerization initiator thereto as needed and performing an emulsion polymerization. In addition to (c), (b) a hydrophobic monomer or the like may be added thereto depending on the types of the desired microencapsulated

pigment and then the resultant mixture may be copolymerized with (c) the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group. The pigment particles used herein may have a hydrophilic group on the surface thereof by surface treatment.

[0018]

Particularly, the microencapsulated pigment according to the invention can be obtained by adding (a) a cationic polymerizable surfactant and (c) the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group to the aqueous dispersion in which the pigment particles having an anionic group on the surfaces thereof are dispersed and polymerizing the resultant mixture. (b) the hydrophobic monomer in addition to (a) and (c) may be added thereto and may be polymerized with (a) and (c).

Here, the anionic polymerizable surfactant means a surfactant having an anionic group, a hydrophobic group, and a polymerizable group and the cationic polymerizable surfactant means a surfactant having a cationic group, a hydrophobic group, and a polymerizable group.

[0019]

In the microencapsulated pigment, the pigment particles having an anionic group on the surfaces thereof

are encapsulated with a polymer having a repeated structure unit derived from the cationic polymerizable surfactant having a cationic group, a hydrophobic group, and a polymerizable group, the anionic polymerizable surfactant having an anionic group, a hydrophobic group, and a polymerizable group, and a hydrophobic monomer.

The microencapsulated pigment can be suitably prepared by the use of a method of adding the cationic polymerizable surfactant to the aqueous dispersion of the pigment particles having an anionic group on the surfaces thereof, adding the hydrophobic monomer and the anionic polymerizable surfactant thereto and then emulsifying the added mixture, and adding a polymerization initiator thereto and performing an emulsion polymerization process thereto.

[0020]

According to the emulsion polymerization process used in the invention, the anionic groups on the surfaces of the pigment particles having the anionic groups on the surfaces thereof are ionically coupled to the cationic groups of the cationic polymerizable surfactant in a polymerization system to form a structure of micell shape in which the anionic groups of the anionic polymerizable surfactant at the outermost shell are oriented to the aqueous phases and a polymer shape is formed by an

additional polymerization reaction. In this way, by forming a specific orientation state in the polymerization system, the monomer existing around the pigment particles before the emulsion polymerization are controlled with very high precision. Accordingly, the microencapsulated pigment according to an embodiment of the invention is capable of preparing an ink for ink jet recording satisfying all the following (1) to (6):

(1) Excellent in dispersion stability;

(2) Excellent in ejection stability from a recording head;

(3) Capable of obtaining recorded matter excellent in fastness of images;

(4) Capable of obtaining recorded matter excellent in print density of images;

(5) Capable of obtaining recorded matter excellent in abrasion resistance of images; and

(6) Capable of obtaining recorded matter in which images are hard to blur, and which is excellent in color developability of images, even when plain paper is used as a recording medium. In the case of a microencapsulated pigment in which a pigment is encapsulated with a polymer previously prepared by phase reversal of emulsion or acid precipitation, a state of pigment particles encapsulated with the polymer is determined by the structure of the

polymer. It is therefore considered that such a state of pigment particles encapsulated with the polymer that all the above-mentioned (1) to (6) are satisfied has not been achieved.

[0021]

Here, it is preferred that the microencapsulated pigment of the invention has an aspect ratio (long-short degree) of 1.0 to 1.3, and a Zingg index of 1.0 to 1.3 (more preferably 1.0 to 1.2), thereby being able to satisfy the above-mentioned (1), (2), (4) and (6) more securely.

When the minor diameter, major diameter and thickness of a particle are taken as  $b$ ,  $l$  and  $t$  ( $l \geq b \geq t > 0$ ), respectively, the aspect ratio (long-short degree) is  $l/b$  ( $\geq 1$ ), the degree of flatness is  $b/t$  ( $\geq 1$ ), and the Zingg index is the long-short degree/the degree of flatness =  $(l \cdot t)/b^2$ . That is, the true sphere has an aspect ratio of 1 and a Zingg index of 1.

When the aspect ratio is larger than 1.3, the microencapsulated pigment becomes flatter in shape to lower the isotropy. This perhaps accounts for the fact that there is a tendency to fail to obtain sufficient results, particularly with respect to the above (1), (2), (4) and (6). Although there is no particular limitation on the method for adjusting the aspect ratio and the Zingg



index within the above-mentioned ranges, the aspect ratio and the Zingg index can be easily satisfied by the microencapsulated pigment encapsulated with the polymer by the emulsion polymerization method.

[0022]

As for microencapsulated pigments prepared by methods other than emulsion polymerization, such as acid precipitation and phase reversal of emulsion, it is difficult to adjust the aspect ratio and the Zingg index within the above-mentioned ranges.

When the microencapsulated pigment is in the range of aspect ratio and Zingg index, the pigment particles have the shape of a true sphere. Accordingly, an ink using the microencapsulated pigment easily becomes Newtonian in its fluid characteristics and is thus excellent in ejection stability of the ink. Further, the microencapsulated pigment particles shaped like a true sphere are arranged at a high density on a recording medium such as paper to reproduce the printing concentration and the color with high efficiency, when the ink lands on the recording medium. Further, the true sphere-shaped pigment particles exhibit excellent dispersibility or dispersion stability.

[0023]

The microencapsulated pigment according to

embodiments of the invention will be described in detail below, with reference to dispersed states of the pigment particles which can occur in the aqueous dispersion in the method for preparing the microencapsulated pigment. The dispersed states of the pigment particles described below include assumptions.

[0024]

(First Embodiment)

A first embodiment provides a microencapsulated pigment formed by adding and emulsifying the anionic polymerizable surfactant to the aqueous dispersion in which the pigment particles are dispersed and adding the polymerizable initiator thereto and performing the emulsion polymerization process thereto.

Fig. 1 is a view showing a state in which pigment particles 21 are dispersed in a solvent containing water as a main component (hereinafter, also referred to as an aqueous medium) and coexists with a polymerizable surfactant 22 having a hydrophilic group 34, a hydrophobic group 32 and a polymerizable group 33. A surfaces 40 of the pigment particles 21 form a hydrophobic region herein. The anionic polymerizable surfactant 22 is adsorbed so that the hydrophobic group 32 is directed toward the pigment particles 21 by an interaction of the hydrophobic group 32 with the surfaces 40. The anionic group 34 of

the anionic polymerizable surfactant 22 is directed in a direction in which the aqueous medium exists, that is, in a direction departing from the pigment particles 1.

[0025]

To such an aqueous dispersion, for example, a polymerization initiator is added to polymerize the polymerizable groups 33 of the polymerizable surfactant 22, thereby preparing a microencapsulated pigment 110 in which the pigment particles 21 are encapsulated with a polymer layer 41, as shown in Fig. 2. A surface of the polymer layer 41 has the anionic group 11, so that the microencapsulated pigment 110 is dispersible in the aqueous medium.

In addition to the anionic polymerizable surfactant 22, a comonomer copolymerizable with the polymerizable surfactant 22 may be allowed to exist in the aqueous dispersion as needed. In this case, the polymer layer 41 can be a copolymer layer in which the polymerizable surfactant 22 and the comonomer are copolymerized with each other.

[0026]

(Second Embodiment)

A second embodiment provides a microencapsulated pigment in which the pigment particles having an anionic group on the surfaces thereof are encapsulated with the

polymer having a repeated structure unit derived from the cationic polymerizable surfactant and a repeated structure unit derived from the anionic polymerizable surfactant.

Fig. 3 is a view showing a state in which pigment particles 1 having an anionic group 14 on the surfaces thereof are dispersed in a solvent containing water as a main component (hereinafter, also referred to as an aqueous medium) and coexists with a cationic polymerizable surfactant 2 having a cationic group 11, a hydrophobic group 12, and a polymerizable group 13 and an anionic polymerizable surfactant 3 having an anionic group 14', a hydrophobic group 12', and a polymerizable group 13'.

The cationic polymerizable surfactant 2 is adsorbed so that the cationic group 11 is directed toward the anionic groups 14 of the pigment particles 1 and they are adsorbed to each other with a strong ionic bond. The hydrophobic groups 12' and the polymerizable group 13' of the anionic polymerizable surfactant 3 are directed to the hydrophobic groups 12 and the polymerizable groups 13 of the cationic polymerizable surfactant 2 by a hydrophobic interaction and the anionic groups 14' of the anionic polymerizable surfactant 3 is directed to a direction in which the aqueous medium exists, that is, in a direction departing from the pigment particles 1.

[0027]

By adding, for example, a polymerization initiator to the aqueous medium and polymerizing the polymerizable groups 13 of the cationic polymerizable surfactant 2 with the polymerizable groups 13' of the anionic polymerizable surfactant 3, as shown in Fig. 4, the microencapsulated pigment 100' in which the pigment particles 1 are encapsulated with a polymer layer 60'. Here, the surface of the polymer layer 60' has the anionic groups 14' and thus the microencapsulated pigment 100' is dispersible in the aqueous medium.

Even when a hydrophilic monomer having an anionic group as a hydrophilic group is used instead of the anionic polymerizable surfactant 3, the microencapsulated pigment can be prepared in the same way. At the time of polymerization, the cationic polymerizable surfactant, the anionic polymerizable surfactant, and/or a comonomer copolymerizable with a hydrophilic monomer having the anionic group may exist in the aqueous dispersion as needed. In this case, the polymer layer may be a copolymer layer which is copolymerized with the cationic polymerizable surfactant, the anionic polymerizable surfactant, and/or the hydrophilic monomer having the anionic group.

[0028]

Other dispersed states which can be taken by the

pigment particles, the cationic polymerizable surfactant, and the anionic polymerizable surfactant according to the second embodiment are shown in Fig. 5.

Fig. 5 is a view showing a state in which the pigment particles 1 having an anionic group 14 on the surfaces thereof are dispersed in a solvent containing water as a main component (hereinafter, also referred to as an aqueous medium) and coexists with a cationic polymerizable surfactant 2 having a cationic group 11, a hydrophobic group 12, and a polymerizable group 13 and an anionic polymerizable surfactant 3 having an anionic group 14', a hydrophobic group 12', and a polymerizable group 13'. The cationic groups 11 of the cationic polymerizable surfactant 2 are directed toward the anionic groups 14 of the pigment particles 1 and they are adsorbed with a strong ionic bond. The hydrophobic groups 12' and the polymerizable groups 13' of the anionic polymerizable surfactant 3 are directed toward the hydrophobic groups 12 and the polymerizable groups 13 of the cationic polymerizable surfactant 2 by a hydrophobic interaction and the anionic groups 14' of another anionic polymerizable surfactant 3 is directed to a direction in which the aqueous medium exists, that is, in a direction departing from the pigment particles 1.

[0029]

A surface of a pigment particle 1 has anionic groups 14 chemically bonded thereto with a specific density and has a hydrophobic region 50 between the anionic groups 14. For example, the hydrophobic groups 12 and the polymerizable groups 13 of the cationic polymerizable surfactant 2 are directed to the hydrophobic region. The anionic groups 14' of the anionic polymerizable surfactant 2 are directed to the cationic groups 11 of the cationic polymerizable surfactant 2 and they are adsorbed to each other with a strong ionic bond. The hydrophobic groups 12' and the polymerizable groups 13' of other anionic polymerizable surfactant 3 are directed toward the hydrophobic groups 12' and the polymerizable groups 13' of the anionic polymerizable surfactant 3 by a hydrophobic interaction and the anionic groups 14' of the anionic polymerizable surfactant 3 are directed to a direction in which the aqueous medium exists, that is, in a direction departing from the pigment particles 1.

[0030]

By adding, for example, a polymerization initiator to the aqueous dispersion and polymerizing the polymerizable groups 13 of the cationic polymerizable surfactant 2 with the polymerizable groups 13' of the anionic polymerizable surfactant 3, as shown in Fig. 6, the microencapsulated pigment 100 in which the pigment

particles 1 are encapsulated with the polymer layers 60 is prepared. Here, since the surfaces of the polymer layers 60 have the anionic groups 14', the microencapsulated pigment 100 is dispersible in the aqueous medium.

When a hydrophilic monomer having an anionic group as a hydrophilic group is used instead of the anionic polymerizable surfactant 3, the microencapsulated pigment can be prepared in the same way. At the time of polymerization, the cationic polymerizable surfactant, the anionic polymerizable surfactant, and/or the comonomer copolymerizable with the hydrophilic monomer having an anionic group may coexist in the aqueous medium as needed. In this case, the polymer layers may be copolymer layers which are copolymerized from the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group and the comonomer.

[0031]

The dispersed states have been described with reference to the drawings. The pigment particles 1 are dispersed in the aqueous medium by arranging the polymerizable surfactant 2 around the pigment particles. In that a wet pigment is used in the pigment particles 1 in the aqueous medium, the pigment particles 1 are finely dispersible compared to an aqueous dispersion in which a dry powder of a pigment is used. According to such a



microencapsulated pigment of the embodiment in which the pigment particles having the hydrophilic group on the surface thereof are encapsulated with the polymer, since the hydrophilic groups on the surface of the microencapsulated pigment are regularly densely orientated in a direction in which the aqueous medium exists as shown in Figs. 2, 4, and 6, it is possible to enhance the dispersion stability of the microencapsulated pigment in the aqueous medium. Accordingly, by using the microencapsulated pigment of the invention as a colorant of the ink for ink jet recording and using an aqueous medium as the solvent of the ink, even when a more weight of microencapsulated pigment is contained in the ink, it is possible to obtain the same dispersion stability as a conventional microencapsulated pigment. When the dispersion stability is excellent, there is reduced the possibility that the microencapsulated pigment clog a nozzle of a recording head, thereby improving the ejection stability. That is, it is possible to prepare an ink of the microencapsulated pigment, which is excellent in dispersion stability and ejection stability and which has an weighted concentration of the colorant compared to a conventional microencapsulated pigment ink. Further, by performing an ink jet recording operation using the ink of the microencapsulated pigment having the high weighted

concentration of the colorant, it is possible to obtain printed matters having high-rigidity images and having high-print-density images.

[0032]

More specifically, in the microencapsulated pigment of the invention, as described above, since the anionic groups derived from the polymerizable surfactant are regularly densely oriented toward the aqueous medium, it is considered that effective electrostatic repulsion occurs between the microencapsulated pigment particles. In addition to the electrostatic repulsion, it is considered that an effect (polymer effect) of spatial disturbance resulting from a polymer of a homopolymer or comonomer of the polymerizable surfactant encapsulating the pigment particles is one reason for the excellent dispersion stability of the microencapsulated pigment of the invention in the aqueous medium.

[0033]

When plain paper is used as the recording medium, blurring is hard to occur in printed images, and the print density of images is also high. The reason for this is considered to be largely due to that the hydrophilic groups are regularly densely orientated toward the aqueous medium. Usually, when the ink is ejected from the recording head and lands on the plain paper, the aqueous

medium rapidly penetrates into the plain paper, but the pigment particles of the conventional pigment ink using the pigment particles dispersed with a dispersant (the pigment particles are coated with the dispersant) also move into the paper together with the aqueous medium and the pigment particles are difficult to be adsorbed on cellulose fiber on a print surface of the plain paper (this is because the amount of the hydrophilic groups on the pigment surface is smaller than that of the microencapsulated pigment according to the invention and the hydrophilic groups are not regularly densely oriented), so that the print density is low, and the color developability also become insufficient.

[0034]

In contrast, the microencapsulated pigment of the invention easily agglomerates by an interaction of the hydrophilic groups (particularly, the anionic groups) existing on the surface of the microencapsulated pigment with various metallic ions such as magnesium, calcium, and aluminum usually contained in the plain paper, or can be easily adsorbed and agglomerates by an interaction of the hydrophilic groups (particularly, the anionic groups) of the microencapsulated pigment with cationic starch and a cationic polymer used together with a sizing agent in sizing treatment of the plain paper. Further, the

microencapsulated pigment is easily adsorbed on a surface of the cellulose fiber by an interaction of the hydrophilic groups (particularly, the anionic groups) with the cellulose fiber. Accordingly, when ink droplets using the microencapsulated pigment of the invention as the colorant are ejected from the recording head and land on the plain paper, the colorant is easily collected in the vicinity of a landing position on the plain paper. Therefore, it is considered that it is possible to high image density and to suppress blurring from occurring.

[0035]

Since the pigment particles are coated with the polymer, the ink for ink jet recording according to the invention has excellent fixability to the recording medium and excellent abrasion resistance of the recorded matter, compared with the conventional ink using surface-processed pigment particles as the colorant.

[0036]

Although it has been described in the first and second embodiments that the microencapsulated pigment is formed by emulsion polymerization, the microencapsulated pigment used in the invention may be formed by mini-emulsion polymerization. The microencapsulated pigment formed by mini-emulsion polymerization can also provide an ink for ink jet recording satisfying (1) to (6) described

above.

Here, the "mini-emulsion polymerization" means that a monomer emulsion is polymerized in the presence of a common surfactant. In the mini-emulsion polymerization, since more stable micells can be formed due to the existence of the common surfactant, it is easy to control the particle size of the microencapsulated pigment and it is thus possible to obtain microencapsulated particles having a uniform particle size. The common surfactant is preferably added at the same time as adding the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group.

[0037]

Known ones used in the "mini-emulsion polymerization" can be usually used as the common surfactant. Examples of the suitable common surfactant can include alkanes such as dodecane, hexadecane, octadecane having 8 to 30 carbon atoms, alkyl alcohols such as lauryl alcohol, cetyl alcoshol, stearyl alcohol having 8 to 30 carbon atoms, alkyl (meth)acrylates such as layryl (meth)acrylate, cetyl (meth)acrylate, stearyl (meth)acrylate, and dodecyl methacrylate having 8 to 30 carbon atoms, alkyl thiols such as layryl mercaptan, cetyl mercaptan, and stearyl mercaptan having 8 to 30 carbon atoms, polymers or polyaducts such as polystyrene and

polymethyl methacrylate, carboxylates, ketones, and amines.

The "mini-emulsion polymerization" is disclosed, for example, in P. L. Tang, E. D. Sudol, C.A. Silebi, M. S. El-Aasser; J. Appl. Polym. Sci., vol. 43, p. 1059 (1991).

[0038]

Next, components of the microencapsulated pigment according to the invention will be described in detail.

The type of the pigment particles according to the invention is not particularly limited, but powder pigment may be used. When the pigment particles are powder pigment, examples of the pigment constituting the pigment particles can include the following inorganic pigments and organic pigments.

The inorganic pigments include carbon blacks (C.I. Pigment Black 7) such as furnace black, lamp black, acetylene black and channel black, and an iron oxide pigment. As the organic pigments, there can be used an azo pigment (including azo lake, an insoluble azo pigment, a condensed azo pigment and a chelate azo pigment), a polycyclic pigment (for example, a phthalocyanine pigment, a perylene pigment, a perinone pigment, an anthraquinone pigment, a quinacridone pigment, a dioxane pigment, a thioindigo pigment, an isoindolinone pigment or a quinoxaline pigment), a dye chelate (for example, a basic dye chelate or an acidic dye chelate), a nitro pigment, a

nitroso pigment or aniline black.

[0039]

More specifically, the inorganic pigments used for black include carbon blacks such as No. 2300, No. 900, MCF88, No. 33, No. 40, No. 45, No. 52, MA7, MA8, MA100 and No. 2200B manufactured by Mitsubishi Chemical Corporation, Raven 5750, Raven 5250, Raven 5000, Raven 3500, Raven 1255 and Raven 700 manufactured by Columbian Chemicals Company, Regal 400R, Regal 330R, Regal 660R, Mogul L, Monarch 700, Monarch 800, Monarch 880, Monarch 900, Monarch 1000, Monarch 1100, Monarch 1300 and Monarch 1400 manufactured by Cabot Corporation, and Color Black FW1, Color Black FW2, Color Black FW2V, Color Black FW18, Color Black FW200, Color Black S150, Color Black S160, Color Black S170, Printex 35, Printex U, Printex V, Printex 140U, Special Black 6, Special Black 5, Special Black 4A and Special Black 4 manufactured by Degussa Corporation.

Further, as the organic pigments for black, there can be used black organic pigments such as aniline black (C.I. Pigment Black 1).

[0040]

Still further, the organic pigments for yellow inks include C.I. Pigment Yellow 1 (hansa yellow), 2, 3 (hansa yellow 10G), 4, 5 (hansa yellow 5G), 6, 7, 10, 11, 12, 13, 14, 16, 17, 24 (flavanthrones Yellow), 34, 35, 37, 53, 55,

65, 73, 74, 75, 81, 83, 93, 94, 95, 97, 98, 99, 108  
(anthrapyrimidine yellow), 109, 110, 113, 117 (copper  
complex pigment), 120, 124, 128, 129, 133  
(quinophthalones), 138, 139 (isoindolinones), 147, 151,  
153 (nickel complex pigment), 154, 167, 172, and 180.

[0041]

Yet still further, the organic pigments for magenta  
inks include C.I. Pigment Reds 1 (para red), 2, 3  
(toluidine red), 4, 5 (1TR red), 7, 8, 9, 10, 11, 12, 14,  
15, 16, 17, 18, 19, 21, 22, 23, 30, 31, 32, 37, 38  
(pyrazolone red), 40, 41, 42, 48 (Ca), 48 (Mn), 57 (Ca),  
57:1, 88 (thioindigo), 112 (naphthol AS), 114 (naphthol  
AS), 122 (dimethyl quinacridone), 123, 144, 146, 149, 150,  
166, 168 (antianthrone orange), 170 (naphthol AS), 171,  
175, 176, 177, 178, 179 (perylene maroon), 184, 185, 187,  
202, 209 (dichloroquinacridone), 219, 224 (perylene), and  
245 (naphthol AS), and C.I. Pigment Violet 19  
(quinacridone), 23 (dioxadine violet), 32, 33, 36, 38, 43  
and 50.

[0042]

Furthermore, the organic pigments for cyan inks  
include C.I. Pigment Blue 1, 2, 3, 15, 15:1, 15:2, 15:3,  
15:34, 15:4, 16 (nonphthalocyanine), 18 (alkali blue  
toner), 22, 25, 60 (threne blue), 65 (violanthrone), and  
66 (Indigo), and C.I. Vat Blue 4 and 60.



[0035]

In addition, as the organic pigments used for color inks other than magenta, cyan, and yellow inks, there can be used C.I. Pigment Green 7 (phthalocyanine green), 10 (green gold), 36, and 37; C.I. Pigment Brawn 3, 5, 25, and 26; and C.I. Pigment Orange 1, 2, 5, 7, 13, 14, 15, 16, 24, 34, 36, 38, 40, 43 and 63.

One or a combination of two or more pigments described above can be used in the microencapsulated pigment according to the invention.

[0044]

The pigment particles used in the invention may be pigment particles having a hydrophilic group on the surfaces thereof. The pigment particles having a hydrophilic group on the surfaces thereof can be suitably prepared by treating the surfaces of the pigment particles with a hydrophilic agent. The group introduced by the surface treatment may be an cationic group or an anionic group. The pigment of the pigment particles having a hydrophilic group on the surfaces thereof is not particularly limited as long as it is not dissolved in the hydrophilic agent, and the above-mentioned examples of the powder pigment may be used.

An example of the hydrophilic agent for treating the surfaces of the pigment particles can include an sulfur-

containing agent.

Examples of the sulfur-containing agent can include sulfuric acid, smoke sulfuric acid, sulfur trioxide, sulfur chloride, sulfur fluoride, sulfur amide, sulfonated pyridine salt, and sulfamic acid and sulfonating agents such as sulfur trioxide, sulfonated pyridine salt, and sulfamic acid are suitable. These agents can be used alone or a combination of two or more (Here, the "sulfonating agent" means an agent for giving sulfonic acid ( $-\text{SO}_3\text{H}$ ) and/or sulfinic acid ( $-\text{RSO}_2\text{H}$ : R is an alkyl group of  $\text{C}_1$  to  $\text{C}_{12}$  or a phenyl group, phenyl groups, or denatures forms thereof)).

[0045]

One is useful which can be complex the sulfur trioxide by a mixture solvent of a solvent (base solvent such as N,N-dimethylformamide, dioxane, pyridine, triethyl amine, and trimethyl amine, nitromethane, acetonitrile, etc.) and one or more solvents to be described later.

Particularly, when the sulfur trioxide itself has such a large reactivity to decompose or denature the pigment itself or it is difficult to control the reaction with strong acid, it is preferable that the surfaces of the pigment particles are treated (sulfonated in this case) using a complex of the sulfur trioxide with third amine.

[0046]

When sulfuric acid, smoke sulfuric acid, sulfur trioxide, sulfur chloride, or sulfur fluoride is used alone, it easily dissolves the pigment particles and thus the reaction need be suppressed with a strong acid reacting with each molecule. In addition, the types and amounts of the solvent to be described later should be noted.

Examples of the solvent used in the reaction can include sulfolane, N-methyl-2-pyrrolidone, dimethyl acetamide, quinoline, hexamethyl phosphotriamide, chloroform, dichloroethane, tetrachloroethane, tetrachloroethylene, dichloromethane, nitromethane, nitrobenzene, liquid sulfur dioxide, carbon disulfide, and trichlorofluoromethane, which do not react with a sulfur-containing agent and are selected from ones in which the pigments are non-soluble or insoluble.

[0047]

The treatment using the sulfur-containing agent is performed by dispersing pigment particles in a solvent, adding the sulfur-containing agent to the dispersion, heating the dispersion at 60 to 200°C, and stirring the dispersion for 3 to 10 hours. Specifically, it is preferable to form a slurry phase (dispersion) by dispersing the mixture at a high speed with a high-speed

mixer in a shearing manner or dispersing the mixture with a beads mill or a jet mill in an impact manner in advance. Thereafter, the dispersion is subjected to a smooth stirring treatment and then the sulfur-containing agent is added thereto, thereby introducing the hydrophilic groups into the surfaces of the pigment particles. At this time, the amount of hydrophilic groups introduced is determined depending on the reaction condition and the type of the sulfur-containing agent. The slurry is subjected to heat treatment and the solvent and the sulfur-containing agent remaining are removed from the slurry of the pigment particles. In the removal, methods such as washing, ultrafiltering, and reverse penetration, centrifuge, and filtration are repeated.

[0048]

By treating the sulfonic acid ( $-\text{SO}_3\text{H}$ ) and/or the sulfinic acid ( $-\text{RSO}_2\text{H}$ : R is an alkyl group of  $\text{C}_1$  to  $\text{C}_{12}$  or a phenyl group, phenyl groups, or denatures forms thereof)) with an alkali compound, it is possible to obtain pigment particles having a sulfonic anionic group ( $-\text{SO}_3^-$ ) and/or a sulfinic anionic group ( $-\text{RSO}_2^-$ : R is an alkyl group of  $\text{C}_1$  to  $\text{C}_{12}$  or a phenyl group, phenyl groups, or denatures forms thereof)). In the invention, the above-mentioned state is preferably used.

[0049]

As the alkali compound, an alkali compound of which a cation becomes an alkali metallic ion or one valent ion represented by chemical formula  $(R_1R_2R_3R_4N)^+$  (where  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  may be equal to or different from each other and indicate a hydrogen atom, an alkyl group, a hydroxyl alkyl group, or a alkyl halide group) is selected. Preferably, the alkali compound is an alkali compound of which a cation is an alkanol amine cation such as a lithium ion ( $Li^+$ ), a potassium ion ( $K^+$ ), a sodium ion ( $Na^+$ ), an ammonium ion ( $NH_4^+$ ), and a triethanol amine cation.

[0050]

A hydroxide anion is suitably used as an anion of the alkali compound and examples thereof can include ammonia, alkanol amine (such as monoethanol amine, diethanol amine, N,N-butylethanol amine, triethanol amine, propanol amine, aminomethyl propanol, and 2-aminoisopropanol), and hydroxide ( $LiOH$ ,  $NaOH$ ,  $KOH$ ) of one valent alkali metal.

[0051]

The amount of added alkali compound is preferably the neutralization equivalent or more of the sulfonic group and/or the sulfinic group of the pigment particles. The amount of volatile additive such as ammonia and alkanol amine is preferably about 1.5 or more time the neutralization equivalent.

[0052]

The treatment can be performed by adding the pigment particles having the sulfonic group and/or the sulfinic group chemically bonded to the surfaces thereof to the alkali compound and shaking the mixture with a paint shaker or the like.

[0053]

A suitable example of the hydrophilic agent for treating the surfaces of the pigment particles is a carboxylating agent. Here, the "carboxylating agent" is an agent for giving a carboxyl group ( $-\text{COOH}$ ).

The carboxylating agent serves to cut and oxidate a partial bond ( $\text{C}=\text{C}$ ,  $\text{C}-\text{C}$ ) on the surface of the pigment particles by the use of an oxidating agent of hypohalous salt such as sodium hypochlorite or potassium hypochlorite. The carboxyl group may be given by physical oxidation such as plasma treatment in addition to the chemical treatment, but a variety of methods may be selected in the invention so long as they can stabilize the dispersion in the aqueous medium. In addition, in the introduction of carboxyl acid, a quinine group or the like may be introduced through it is quantitatively small. This case is not against the gist of the invention so long as the dispersion stability of the microencapsulated pigment in the aqueous medium can be secured.

[0054]

In the carboxylation of the carboxylating agent, for example, it is preferable to form a slurry phase (dispersion) by dispersing the pigment particles in the aqueous medium at a high speed with a high-speed mixer in a shearing manner or dispersing the pigment particles in the aqueous medium with a beads mill or a jet mill in an impact manner in advance. Hypohalous salt such as sodium hypochlorous having an effective halogen concentration of 10 to 30% is mixed into an appropriate amount of water, the mixture is heated at 60°C to 80°C, and the mixture is stirred for 5 to 10 hours and preferably for 10 hours or more. This treatment accompanies with a considerable amount of heat and thus safe notice is necessary. Thereafter, the slurry is subjected to heat treatment and the solvent and the carboxylating agent remaining are removed from the slurry of the pigment particles having been subjected to the surface treatment. The methods such as washing, ultrafiltering, and reverse penetration, centrifuge, and filtration are repeated to form an aqueous dispersion.

[0055]

Here, By treating the pigment particles having a carboxyl group (-COOH) with an alkali compound, it is possible to prepare pigment particles having a carboxyl

anionic group (-COOH) as a hydrophilic group on the surfaces thereof. This state is preferably used in the invention.

The types of the alkali compound and the processing method using the alkali compound are as described above.

[0056]

Next, a technique for inspecting a preferable amount of a hydrophilic group introduced onto the surfaces of the pigment particles and an introduced state thereof will be described.

First, when hydration is performed using a sulfonating agent, the amount of hydrophilic groups introduced onto the surfaces of the pigment particles is preferably 0.01 mmol/g or more of the pigment particles. When the amount of introduced hydrophilic groups is less than 0.01 mmol/g, agglomerated pigment particles can easily occur in the process of microencapsulating the pigment particles in the aqueous medium and the average particle size of the microencapsulated pigment tends to increase. With the increase in average particle size of the microencapsulated pigment, the dispersion stability and the ejection stability are improved but it is difficult to obtain the ink for ink jet recording capable of enhancing the print density of an image.

The upper limit of the amount of hydrophilic groups



introduced into the pigment particles is not particularly limited, but when the upper limit is greater than 0.15 mmol/g, the variation in average particle size accompanied with the increase in the amount of introduced hydrophilic groups may not be recognized and thus it is preferable in view of cost that the upper limit is 0.15 mmol/g or less.

[0057]

Next, the amount of hydrophilic groups introduced into the surfaces of the pigment particles by the carboxylating agent will be described. In the surface treatment used in the invention, it is considered that the carboxyl group ( $\text{-COOH}$ ) and/or the carboxyl anionic group ( $\text{-COO}^-$ ) is introduced onto the surfaces of the pigment particles. However, since the introduced amount cannot be obtained directly, a surface active hydrogen content is measured as the introduced amount in the invention. The detailed measuring method will be described later.

The active hydrogen content with respect to the pigment obtained in such a way is preferably 1.0 mmol/g or more and more preferably 1.5 mmol/g or more. When the content is less than 1.0 mmol/g, water dispersibility is deteriorated and the agglomeration (that particles are naturally collected to increase the particle size) in the microencapsulating process can easily occur.

[0058]

Although the pigment particles having a hydrophilic group on the surfaces thereof have been described, the average particle size of the pigment particles having a hydrophilic group on the surfaces thereof can be easily made to be 150 nm or less by the above-mentioned method. Particularly, by selecting the types of the pigment or the hydrophilic agent, the amount of introduced hydrophilic groups, and the like, the average particle size is preferably in the range of 20 nm to 80 nm. As a result, it is possible to obtain a microencapsulated pigment which can more surely prepare an ink for ink jet recording which is excellent in dispersion stability and ejection stability and enhances the print density of an image.

[0059]

The pigment particles according to the invention may be in the form of wet pigment. Here, the "wet pigment" contains water of 40 to 80% by weight in the state right before the final drying step in a known pigment preparing process (see Japanese Unexamined Patent Application Publication Nos. 9-288378 and 9-288379). Usually, the pigment particles are prepared as powdered pigment particles by drying in the preparation process, but agglomeration of the pigment particles proceeds with a decrease in water content to increase the particle size of the pigment particles in the process of drying.

Specific examples of the wet pigment are described as follows. Examples of the pigments constituting the wet pigment include various wet pigments such as organic pigments such as a Monoazo Yellow pigment, a Disazo Yellow pigment, a carmine pigment, a rhodamine pigment, a quinacridone pigment, a phthalocyanine pigment, an anthraquinone pigment, a thioindigo pigment, a perinone pigment, a perylene pigment, a dioxane pigment, a quinophthalone pigment, an isoindolinone pigment, and a benzimidazolone pigment, and carbon blacks. In the invention, C.I. Pigment Red 48:1, C.I. Pigment Red 122, C.I. Pigment Yellow 17, and C.I. Pigment Blue 15:3 are particularly preferably used.

[0060]

(1) Azo Pigment

The azo pigment is obtained by the coupling reaction of a diazonium salt with a coupling component (such as a  $\beta$ -naphthol derivative showing keto-enol type tautomerism, an acetoacetic acid anilide derivative or a pyrazolone derivative). The coupling reaction is conducted in the presence of an alkali compound, and a solution after the reaction contains an azo pigment, a salt and water. The solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after

the reaction, and washing the azo pigment in a wet state with water is also usable as the wet pigment of this embodiment.

[0061]

## (2) Phthalocyanine Pigment

The phthalocyanine pigment is obtained by conducting a pigmentation process such as a sulfuric acid process (a process for modifying the crystal form, the form of primary particles and the particle size distribution of a crude pigment to develop physical properties as a colorant) to a crude pigment (which is an acicular crystalline material, and cannot be used as it is) obtained by a phthalic anhydride process or a phthalodinitrile process. As the sulfuric acid processes, there have been known an acid pasting process and an acid slurry process.

In the acid pasting process, the crude pigment is dissolved in sulfuric acid having a concentration of 95% or more, and the resulting solution is poured into a large amount of water to precipitate the phthalocyanine pigment as fine particles. This solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing the azo pigment in a wet state with water is also usable as

the wet pigment of this embodiment (a wet cake described in JP 9-279052 A, a pigment paste described in JP 2002-265812 A, or the like)

In the acid slurry process, the crude pigment is added to sulfuric acid having a concentration of 60 to 90%, followed by stirring to form crystals of phthalocyanine sulfate, which are poured into a large amount of water to precipitate the phthalocyanine pigment as fine particles. This solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing the phthalocyanine pigment in a wet state with water is also usable as the wet pigment of this embodiment (a pigment cake described in JP 8-217986 A, or the like).

[0062]

### (3) Polycyclic Pigment

#### (3-1) Quinacridone Pigment

As the preparation of the quinacridone pigment, there has been known a process for obtaining it by oxidation of dihydroquinacridone. In this case, the solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing the quinacridone pigment in a

wet state with water is also usable as the wet pigment of this embodiment.

[0063]

(3-2) Isoindolinone Pigment

The isoindolinone pigment is obtained by reacting 1 mole of an isoindolinone derivative with 2 moles of an aromatic diamine. The solution after the reaction and a concentrate thereof are usable as the wet pigment of this embodiment. Further, a product of the state after filtering the solution after the reaction, and washing the isoindolinone pigment in a wet state with water is also usable as the wet pigment of this embodiment.

[0064]

(3-3) Perylene Pigment

The perylene pigment is obtained by a process comprising (i) reacting perylenetetracarboxylic acid diimide with sulfuric acid to prepare C.I. Pigment Red 224 (the first step) and then, reacting C.I. Pigment Red 224 with an aniline derivative (the second step), or (ii) reacting perylenetetracarboxylic acid diimide with an alkyl chloride.

In (i), the solution after the first step and a concentrate thereof are usable as the wet pigment (C.I. Pigment Red 224) of this embodiment. Further, a product of the state after filtering the solution after the

reaction, and washing C.I. Pigment Red 224 in a wet state with water is also usable as the wet pigment of this embodiment. Furthermore, the solution of the second step and a concentrate thereof are usable as the wet pigment of this embodiment. Moreover, a product of the state after filtering the solution after the reaction, and washing the perylene pigment in a wet state with water is also usable as the wet pigment of this embodiment.

[0065]

Further, pigment cakes before drying in processes for preparing disazo lake pigments described in Japanese Unexamined Patent Application Publication Nos. 5-9399, 5-9400, 5-65426, 7-126545, and 9-217017 are usable as the wet pigments of this embodiment.

[0066]

Furthermore, commercially available products usable as the wet pigments in this embodiment include an aqueous Lithol (registered trade mark)-Rubine-pigment suspension (C.I. 15850) and a Heliogen (registered trade mark)-blue-pigment cake (C.I. 74160).

[0067]

In an aqueous dispersion of the microencapsulated pigment of the invention, the use of the wet pigment as described above allows the average particle size of pigment particles to be easily adjusted to 150 nm or less,

thereby being able to impart excellent dispersibility, dispersion stability and ejection stability to the ink for ink jet recording using the microencapsulated pigment of the invention, and to increase the print density of images. When a general powder pigment is used, the particle size of the resulting microencapsulated pigment is liable to become large, which causes poor dispersibility, dispersion stability and ejection stability of the ink, and the print density of printed matter tends to decrease (in this specification, the description of the average particle size is described based on measured values by a laser light scattering process).

[0068]

Next, components ((a) cationic polymerizable surfactant, (b) hydrophobic monomer, (c) anionic polymerizable surfactant and/or hydrophilic monomer, and other comonomers) of the coating polymer of the microencapsulated pigment will be described.

First, a cationic group selected from a group consisting of a first amine cation, a second amine cation, a third amine cation, and a fourth grade ammonium cation is preferably used as the cationic group of the cationic polymerizable surfactant. An example of the first amine cation is a monoalkyl ammonium cation ( $\text{RNH}_3^+$ ), an example of the second amine cation is a dialkyl ammonium cation



( $R_2NH_2^+$ ), an example of the third amine cation is a trialkyl ammonium cation ( $R_3NH^+$ ), and an example of the fourth grade ammonium cation is  $R_4N^+$ . Here, R is a hydrophobic group or a polymerizable group and is represented by the followings.

Examples of a counter anion of the cationic group can include  $Cl^-$ ,  $Br^-$ , and  $I^-$ .

One selected from a group consisting of an alkyl group, an aryl group, and a group combining them is preferably used as the hydrophobic group.

The polymerizable group is preferably an unsaturated hydrocarbon group, and more particularly, one selected from the group consisting of a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, a propenyl group, a vinylidene group and a vinylene group. Of these, an acryloyl group and a methacryloyl group are particularly preferable.

[0069]

An example of the cationic polymerizable surfactant includes cationic allyl derivatives described in Japanese Examined Patent Application Publication No. 4-65824.

[0070]

Examples of the cationic polymerizable surfactant used in the invention can include compounds expressed by a general formula  $R_{[4-(1+m+n)]}R_1^1R_m^2R_n^3N^+X^-$  (where R is a

polymerizable group,  $R^1$ ,  $R^2$ , and  $R^3$  are an alkyl group or an aryl group, X is Cl, Br, or I, l, m, and n are 1 or 0). Here, a suitable example of the polymerizable group is a hydrocarbon group having an unsaturated hydrocarbon group radically polymerizable and specific examples thereof can include an allyl group, an acryloyl group, a methacryloyl group, a vinyl group, a propenyl group, a vinylidene group, and a vinylene group.

[0071]

Specific examples of the cationic polymerizable surfactant can include methacrylic dimethylaminoethylmethyl chloride, methacrylic dimethylaminoethylbenzyl chloride, methacryloyl oxyethyltrimethyl ammonium chloride, diallyldimethyl ammonium chloride, and 2-hydroxy-3-methacryloxypropyl trimethyl ammonium chloride.

[0072]

As the cationic polymerizable surfactants, there can also be used commercially available products. Examples thereof include Acrylester DMC (made by Mitsubishi Rayon Co., Ltd.), Acrylester DML60 (made by Mitsubishi Rayon Co., Ltd.), and C-1615 (made by Daiichi Kogyo Seiyaku Co., Ltd.).

[0073]

The above-mentioned cationic polymerizable

surfactants can be used alone or as a mixture of two or more.

[0074]

The amount of added cationic polymerizable surfactant is preferably in the range of 0.5 to 2 time the total number of moles (=weight of used pigment (g) × anionic group of pigment surface (mol/g)) of the anionic groups with respect to the use amount of the pigment having an anionic group on the surface thereof and more preferably in the range of 0.8 to 1.2 time the molarity thereof. By setting the added amount to 0.5 time or more the molarity thereof, the surfactant is strongly ionically bonded to the pigment particles having an anionic group as the hydrophilic group, thereby easily encapsulating the pigment particles. By setting the added amount to 2 time or less the molarity thereof, the occurrence of the cationic polymerizable surfactant not adsorbed to the pigment particles can be reduced, thereby preventing polymer particles (particles including only polymers) not having the pigment particles as a core material from occurring.

[0075]

Specific examples of the anionic polymerizable surfactants include anionic allyl derivatives described in Japanese Examined Patent Application Publication Nos. 49-46291 and 1-24142 and Japanese Unexamined Patent

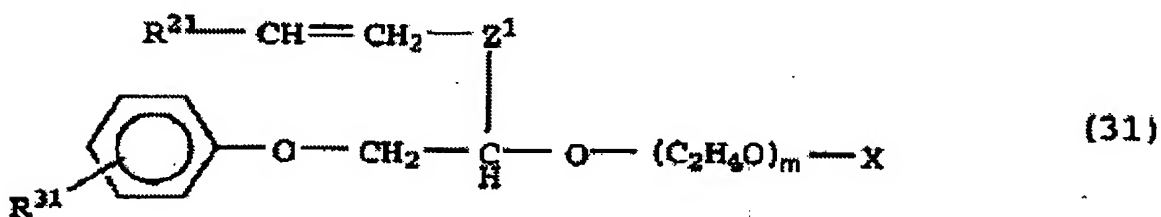
Application Publication No. 62-104802, anionic propenyl derivatives described in Japanese Unexamined Patent Application Publication No. 62-221431, anionic acrylic acid derivatives described in Japanese Unexamined Patent Application Publication Nos. 62-34947 and 55-11525, and anionic itaconic acid derivatives described in Japanese Examined Patent Application Publication No. 46-34898 and Japanese Unexamined Patent Application Publication Nos. 51-30284.

[0076]

The anionic polymerizable surfactant used in the invention is expressed by general formula (31).

[0077]

[Kagaku 1]



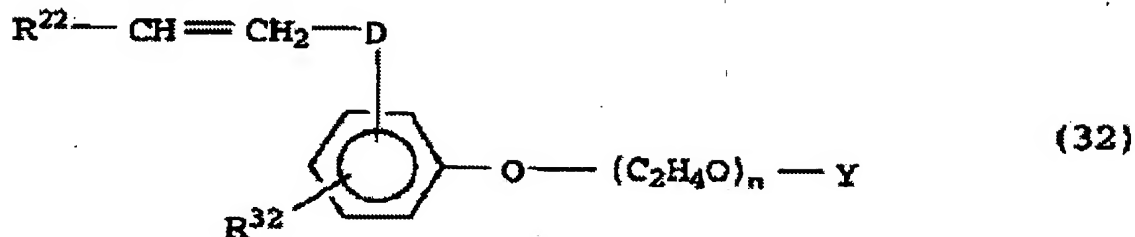
[0078]

where  $\text{R}^{21}$  and  $\text{R}^{31}$  are each independently a hydrogen atom or a hydrocarbon group having 1 to 12 carbon atoms;  $\text{Z}^1$  is a group represented by a carbon-carbon single bond or formula  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ;  $m$  is an integer of 2 to 20; and  $\text{X}$  is a group expressed by formula  $-\text{SO}_3\text{M}^1$ , wherein  $\text{M}^1$  is an alkali metal, an ammonium salt or an alkanolamine; and a compound

represented by general formula (32).

[0079]

[Kagaku 2]



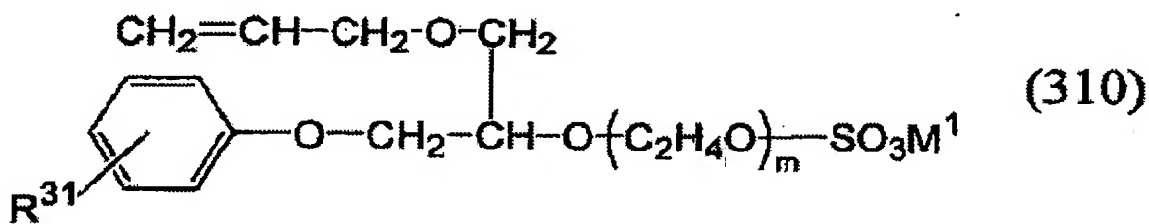
wherein  $\text{R}^{22}$  and  $\text{R}^{32}$  are each independently a hydrogen atom or a hydrocarbon group having 1 to 12 carbon atoms;  $\text{Z}^2$  is a group represented by a carbon-carbon single bond or formula  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ;  $n$  is an integer of 2 to 20; and  $\text{Y}$  is a group expressed by formula  $-\text{SO}_3\text{M}^2$ , wherein  $\text{M}^2$  is an alkali metal, an ammonium salt or an alkanol amine.

[0080]

The polymerizable surfactants represented by the above-mentioned formula (31) are described in JP 5-320276 A and JP 10-316909 A. It is possible to adjust the adsorbability onto the surface of the pigment particle and the hydrophilicity of the surface of the pigment particle by appropriately adjusting the kind of  $\text{R}^{21}$  and the value of  $i$ . Preferred specific examples of the polymerizable surfactants represented by the following formula (310) include compounds represented by the following formulas (31a) to (31d).

[0081]

[Kagaku 3]

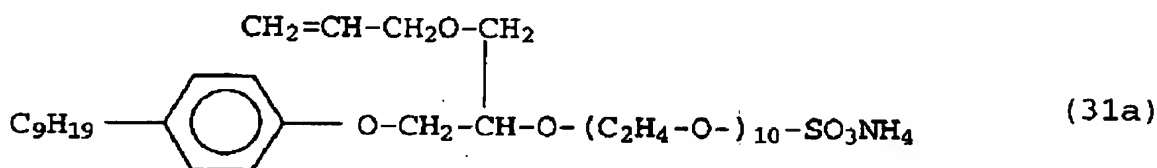


[0082]

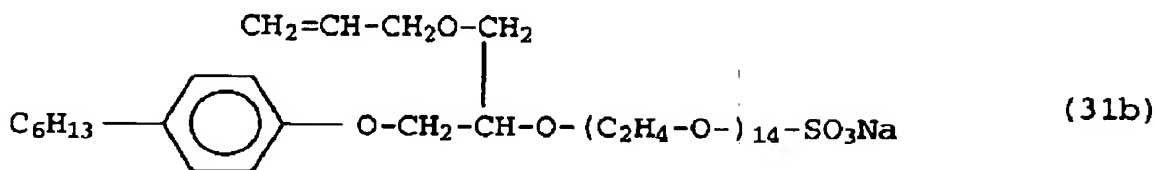
In the formula, R<sup>31</sup>, m, and M<sup>1</sup> are equal to those of the compound expressed by formula (31).

[0083]

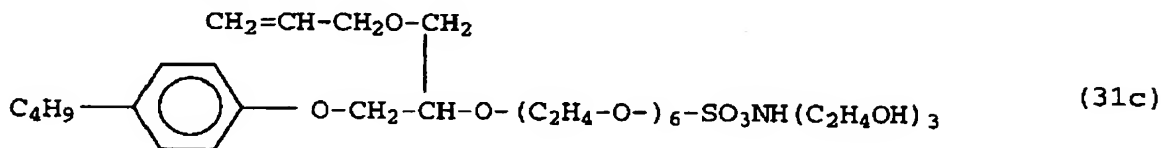
[Kagaku 4]



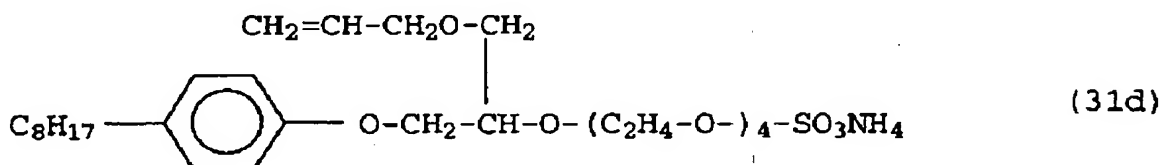
[Kagaku 5]



[Kagaku 6]



[Kagaku 7]



[0084]

As the above-mentioned anionic polymerizable surfactants, there can also be used commercially available products. Examples thereof include Aqualon HS series (Aqualon HS-05, HS-10, HS-20 and HS-1025) made by Daiichi Kogyo Yakuhin Co., Ltd. and Adeka Reasoap SE series SE-10N and SE-20N made by Asahi Denka Co., Ltd.

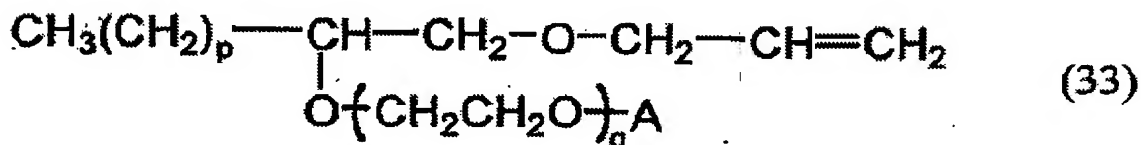
Adeka Reasoap SE-10N made by Asahi Denka Co., Ltd. is a compound in which  $M^1$  is  $NH_4$ ,  $R^{31}$  is  $C_9H_{19}$ , and  $m=10$  in the compounds expressed by formular (310). Adeka Reasoap SE series SE-20N made by Asahi Denka Co., Ltd. is a compound in which  $M^1$  is  $NH_4$ ,  $R^{31}$  is  $C_9H_{19}$ , and  $m=20$  in the compounds expressed by formular (310).

[0085]

As the anionic polymerizable surfactant used in the invention is expressed by the following general formula (33).

[0086]

[Kagaku 8]

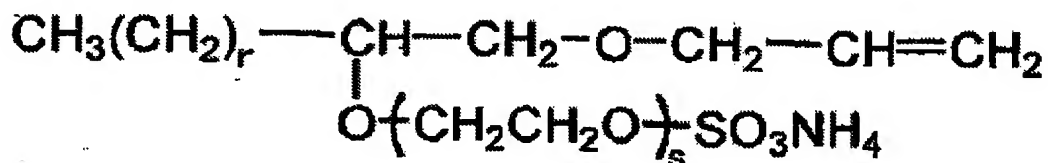


[where  $p$  is 9 or 11;  $q$  is an integer of 2 to 20; and  $A$  is a group expressed by  $-SO_3M^3$ , wherein  $M^3$  is an alkali metal,

an ammonium salt, or an alkanolamine.] Preferred specific examples of the polymerizable surfactants expressed by formula (33) include the following compound.

[0087]

[Kagaku 9]



[where r is 9 or 11 and s is 5 or 10.]

[0088]

As the above-mentioned anionic polymerizable surfactants, there can also be used commercially available products. Examples thereof include Aqualon KH series (Aqualon KH-05 and KH-10) made by Daiichi Kogyo Yakuhin Co., Ltd. Aqualon KH-5 is a compound in which r is 9 and s is 5 in the compounds expressed by the above mentioned formula and a compound in which r is 11 and s is 5. Aqualon KH-10 is a mixture of a compound in which r is 9 and s is 10 in the compounds expressed by the above mentioned formula and a compound in which r is 11 and s is 10.

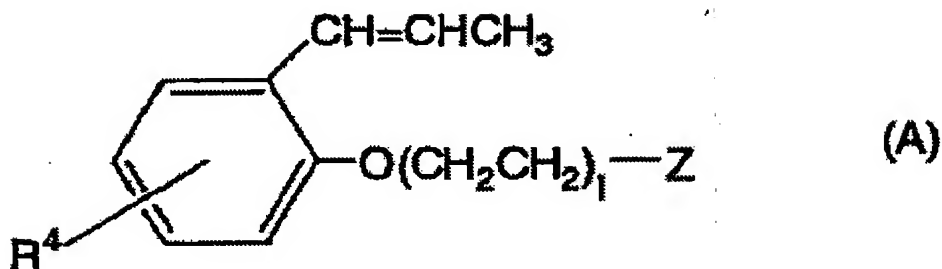
[0089]

A compound expressed by the following formula (A) is preferably used as the anionic polymerizable surfactant.

[0090]



[Kagaku 10]



**Z; -SO<sub>3</sub>M<sup>4</sup>**

[where R<sup>4</sup> denotes an hydrogen atom or a hydrocarbon having 1 to 12 carbon atoms, l denotes a number in the range of 2 to 20, and M<sup>4</sup> denotes an alkali metal, an ammonium salt, or alkanol amine.]

[0091]

The anionic polymerizable surfactants described above can be used alone or as a mixture of two or more.

[0092]

The amount of the added anionic polymerizable surfactant is preferably in the range of 5 to 70% by part and more preferably in the range of 10 to 50% by part, based on 100% by part of the pigment. By adding the anionic polymerizable surfactant by 5% by part or more, the dispersibility is excellent and the ejection stability is also excellent. The adsorbability to paper fiber is improved, thereby resulting in excellent print density and color developability. Furthermore, by adding the

polymerizable surfactant by 70% by part or less, the occurrence of the anionic polymerizable surfactant not adsorbed to the pigment particles can be reduced.

When the anionic polymerizable surfactant and the cationic polymerizable surfactant are used together, the amount of the added anionic polymerizable surfactant is preferably in the range of 1 to 10 time and more preferably in the range of 1.0 to 5 time the molarity of the cationic polymerizable surfactant. By adding the anionic polymerizable surfactant by 1 time or more the molarity, the dispersibility and the dispersion stability of the encapsulated particles are excellent and the ejection stability is also excellent. The adsorbability to paper fiber is improved, thereby resulting in excellent print density and color developability. By adding the anionic polymerizable surfactant by 10 time or less the molarity thereof, the occurrence of the anionic polymerizable surfactant not contributing to the encapsulation can be reduced, thereby preventing polymer particles other than the encapsulated particles from occurring.

[0093]

The anionic group of the anionic polymerizable surfactant is considered as being oriented toward the liquid phase on the surfaces of the encapsulated particles

after the microencapsulation. Accordingly, the dispersibility and the dispersion stability of the encapsulated particles in the liquid phase are excellent. The anionic group easily interacts with various metal ions such as magnesium, calcium, and aluminum, cationic starch, and cationic polymers which are usually contained in plain paper, and also easily interact with a surface of cellulose fiber. Accordingly, when the ink for ink jet recording using the microencapsulated pigment as a colorant is ejected on the plain paper, the colorant is easily collected in the vicinity of a landing position on the plain paper. Accordingly, high image density is obtained more reliably, and blurring can also be inhibited from occurring in images.

[0094]

The hydrophilic monomer having an anionic group used in the invention has at least an anionic group and a polymerizable group as the hydrophilic group in its structure and the hydrophilic group thereof can be preferably selected from a group consisting of a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group, and salts of these groups.

The polymerizable group is an unsaturated hydrocarbon group radically polymerizable and is preferably selected from a group consisting of a vinyl

group, an allyl group, an acryloyl group, a methacryloyl group, a propenyl group, a vinylidene group, and a vinylene group.

[0095]

The anionic group such as a sulfonic acid group, a sulfinic acid group, a carboxyl group, a carbonyl group, and salts of these groups is considered as existing oriented toward the liquid phase on the surfaces of the encapsulated particles and thus the dispersibility and the dispersion stability of the encapsulated particles in the liquid phase are excellent. The anionic group easily interacts with various metal ions such as magnesium, calcium, and aluminum, cationic starch, and cationic polymers which are usually contained in plain paper, and also easily interact with a surface of cellulose fiber. When the microencapsulated pigment is prepared using the polymerizable monomer having an anionic group as the hydrophilic group and the ink for ink jet recording using the microencapsulated pigment as a colorant is ejected to the plain paper, the colorant is easily collected in the vicinity of a landing position on the plain paper. Accordingly, the print density of an image can be obtained more reliably and the blurring can be prevented from occurring.

Preferably examples of the hydrophilic monomer

having an anionic group can include methacrylate, acrylate, (meth)acrylate containing a phosphate group, sodium vinylsulfonate, 2-sulfoethylmethacrylate, and 2-acrylamid-2-methylpropanesulfonate.

[0096]

The amount of the hydrophilic monomer having an anionic group is preferably in the range of 1 to 10 time and more preferably in the range of 1.0 to 5 time the molarity of the cationic polymerizable surfactant. By adding the hydrophilic monomer by 1 time or more the molarity, the dispersibility and the dispersion stability of the encapsulated particles are excellent and the ejection stability is also excellent. By adding the hydrophilic monomer by 10 time or less the molarity, the occurrence of the hydrophilic monomer not contributing to the encapsulation can be reduced, thereby preventing polymer particles other than the encapsulated particles from occurring.

[0097]

When the cationic polymerizable surfactant and the hydrophilic monomer having an anionic group are used together, the total added amount thereof is preferably in the range of 1 to 10 time and more preferably in the range of 1.0 to 5 time the molarity of the cationic polymerizable surfactant. As described above, by

adjusting the total added amount to 1 time or more the molarity, the dispersibility and the dispersion stability of the encapsulated particles are excellent and the ejection stability is also excellent. By adjusting the total added amount to 10 time or less the molarity thereof, the occurrence of the anionic polymerizable surfactant not contributing to the encapsulation can be reduced, thereby preventing polymer particles other than the encapsulated particles from occurring.

[0098]

In addition, another commoner may be added thereto so as to control the fixability to the recording medium and the abrasion resistance or the medium resistance thereof or to control the storage stability of the ink.

As the another commoner, a hydrophilic monomer (hydrophilic monomer other than the hydrophilic monomer having an anionic group) and/or a hydrophobic monomer can be used.

In particular, the fixability to the recording medium and the abrasion resistance can be improved by controlling the glass transition temperature ( $T_g$ ) of a copolymer covering the pigment particles of the microencapsulated pigment according to the invention.

At the room temperature, when an image is printed on plain paper or a recording medium such as a specific

medium for ink jet recording with the ink using the microencapsulated pigment according to the invention, the water medium (including water an/or a water-soluble organic medium) around the pigment particles of the microencapsulated pigment according to the invention invades into the plain paper or the recording medium such as a specific medium for ink recording and thus is removed from the vicinity of the pigment particles of the microencapsulated pigment, thereby allowing the pigment particles of the microencapsulated pigment to approach each other. At this time, when the glass transition temperature ( $T_g$ ) of the copolymer covering the pigment particles of the microencapsulated pigment is lower than the room temperature, the copolymer covering the pigment particles of the microencapsulated pigment coats the pigment with the pigment encapsulated by means of a capillary pressure generated in a gap between the microencapsulated pigment particles, thereby particularly improving the fixability and the abrasion resistance of an image.

[0099]

Generally, when the temperature of a polymer solid, specifically, an amorphous polymer solid, rises from a low temperature to a high temperature, a state (glass state) requiring form a slight deformation is changed to a

state in which a large deformation occurs with a small force. The temperature at which such a phenomenon occurs is referred to as a glass transition point (or glass transition temperature). Generally, in a differential heat curve obtained by measuring the temperature with a differential scanning calorimeter, a temperature intersecting a base line when a tangential line is drawn from the bottom of an endothermic peak to a start point of the endothermic process is set as the glass transition point.

It is known that other physical properties such as elastic index, specific heat, and refractive index are abruptly changed at the glass transition temperature, and thus the glass transition point is determined by measuring the physical properties. In the invention, the glass transition temperature obtained by measuring the increase in temperature with the differential scanning calorimeter (DSC) is used.

At the glass transition temperature, in order to form a film with the microencapsulated pigment according to the invention at a room temperature when an image is printed on plain paper or a recording medium such as a specific medium for ink jet recording with the ink using the microencapsulated pigment according to the invention, the glass transition point ( $T_g$ ) of the copolymer covering



the pigment particles of the microencapsulated pigment is preferably 30°C or less, more preferably 15°C or less, and still more preferably 10°C or less. Accordingly, the copolymer covering the pigment particles of the microencapsulated pigment is preferably designed to have a glass transition point of 30°C or less, more preferably 15°C or less, and still more preferably 10°C or less. However, the glass transition point is less than -20°C, the medium resistance tends to be lowered.

[0100]

The glass transition point of the copolymer can be set within the range by properly selecting the types and the composition ratio of the hydrophobic monomer to be used. When the printed matter can be heated to a temperature higher than the glass transition point (T<sub>g</sub>) of the copolymer covering the pigment particles of the microencapsulated pigment, the film formation is possible with the glass transition temperature lower than the heated temperature. Accordingly, there is no problem when the glass transition temperature is higher than 30°C, but it is necessary to additionally provide a heating mechanism to an ink jet recording apparatus in this case, thereby causing an increase in cost. As a result, it is preferable that the glass transition temperature is 30°C or less.

[0101]

The hydrophilic monomer other than the hydrophilic monomer having an anionic group can have a hydrophilic group such as a hydroxide group, an ethylenoxide group, an amide group, and an amino group. The above-mentioned hydrophilic groups are considered as existing oriented toward the liquid phase on the microencapsulated pigment particles along with the anionic groups and can easily form a hydrogen bond with an OH group of cellulose fiber of the paper. Accordingly, when the ink for ink jet recording using the microencapsulated pigment obtained using the hydrophilic monomer having the hydrophilic group together as a colorant is ejected to the plain paper, the colorant can be more easily adsorbed on the cellulose fiber of the plain paper and thus easily stay in the vicinity of a landing position and in the vicinity of the surface of the plain paper. Accordingly, it is possible to to further improve the print density of an image and to suppress the blurring from occurring.

[0102]

Examples of the hydrophilic monomer other than the hydrophilic monomer having an anionic group can include alkylaminoesters of an acrylic acid or methacrylic acid such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, and 2-hydroxybutyl methacrylate having an OH

group, ethyldiethylen glycol acrylate, polyethylene glycol monomethacrylate, and methoxy polyethylene glycol acrylate having an ethylenoxide group, acryl amide and N,N-dimethyl acrylamide methacrylate having an amide group, N-methylaminoethyl methacrylate, N-methylaminoethyl acrylate, dimethylaminoethyl methacrylate, and diethylaminoethyl methacrylate having an amino group; unsaturated amides having an alkylamino group such as N-(2-dimethylaminoethyl)acryl amide, N-(2-dimethylaminoethyl)methacryl amide, and N,N-dimethylaminopropyl acryl amide; monovinyl pyrimidines such as vinyl pyrimidine; vinyl ethers having an alkyl amino group such as dimethylaminoethyl vinyl ether; vinyl imidazol; and N-vinyl-2-pyrrolidone.

[0103]

A hydrophobic monomer can be properly used to satisfy the requirements such as the fixability, the abrasion resistance, the water resistance, the medium resistance of the printed matter. That is, in the microencapsulated pigment according to the invention, the pigment particles having an anionic group on the surfaces thereof may additionally have a repeated structure unit derived from a hydrophobic monomer, in addition to the repeated structure unit derived from the cationic polymerizable surfactant having a cationic group, a

hydrophobic group, and a polymerizable group and the repeated structure unit derived from the anionic polymerizable surfactant having an anionic group, a hydrophobic group, and a polymerizable group.

[0104]

The hydrophobic monomer has at least a hydrophobic group and a polymerizable group in its structure and the hydrophobic group is suitably selected from a group consisting of an aliphatic hydrocarbon group, an alicyclic hydrocarbon group, and an aromatic hydrocarbon group. Examples of the aliphatic hydrocarbon group can include a methyl group, an ethyl group, and a propyl group, examples of the alicyclic hydrocarbon group can include a cyclohexyl group, a dicyclopentenyl group, a dicyclopentanyl group, and an isobornyl group, and examples of the aromatic hydrocarbon group can include a benzyl group, a phenyl group

The polymerizable group is an unsaturated hydrocarbon group radically polymerizable and is preferably selected from a group consisting of a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, a propenyl group, a vinylidene group, and a vinylene group.

[0105]

Specific examples of the hydrophobic monomer include

styrene derivatives such as styrene, methyl styrene, dimethyl styrene, chlorostyrene, dichloro styrene, bromo styrene, p-chloromethyl styrene, and divinyl benzene; mono-functional acrylic esters such as methyl acrylate, ethyl acrylate, n-butyl acrylate, butoxy ethyl acrylate, benzyl acrylate, phenyl acrylate, phenoxyethyl acrylate, cyclohexyl acrylate, dicyclopentanyl acrylate, dicyclopentenyl acrylate, dicyclopentenylloxyethyl acrylate, tetrahydrofurfuryl acrylate, and isobornyl acrylate; mono-functional methacrylic esters such as methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, butoxymethyl methacrylate, benzyl methacrylate, phenyl methacrylate, phenoxyethyl methacrylate, cyclohexyl methacrylate, dicyclopentanyl methacrylate, dicyclopentenyl methacrylate, dicyclopentenylloxyethyl methacrylate, tetrahydrofurfuryl methacrylate, and isobornyl methacrylate; allyl compounds such as allyl benzene, allyl-3-cyclohexane propanate, 1-allyl-3,4-dimethoxy benzene, allyl phenoxyacetate, allyl phenoxyacetate, allyl phenylacetate, allylcyclohexane, and multi-valent allyl carboxylate; esters of fumaric acid, maleic acid, and itaconic acid; and radically polymerizable group-containing monomers such as N-substituted maleimide and cyclic olefin.

[0106]

The hydrophobic monomer can be selected so as to satisfy the requirements and added amounts thereof are properly determined.

[0107]

Further, a crosslinking monomer can also be used in the invention. The crosslinking monomer usable in the invention is a compound having two or more of unsaturated hydrocarbon groups of at least one kind selected from the group consisting of a vinyl group, an allyl group, an acryloyl group, a methacryloyl group, a propenyl group, a vinylidene group and a vinylene group. Examples thereof include ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, polyethylene glycol diacrylate, allyl acrylate, bis(acryloxyethyl)hydroxyethyl isocyanurate, bis(acryloxyneopentyl glycol) adipate, 1,3-butylene glycol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, propylene glycol diacrylate, polypropylene glycol diacrylate, 2-hydroxy-1,3-diacryloxy propane, 2,2-bis[4-(acryloxy)phenyl]propane, 2,2-bis[4-(acryloxyethoxy)phenyl]propane, 2,2-bis[4-(acryloxyethoxydiethoxy)phenyl]propane, 2,2-bis[4-(acryloxyethoxy polyethoxy)-phenyl]propane, hydroxyl pivalic acid neopentyl glycol diacrylate, 1,4-butanediol diacrylate, dicyclopentanyl diacrylate, dipentaerythritol hexaacrylate,

dipentaerythritol monohydroxypentaacrylate,  
 ditrimethylolpropane tetraacrylate, pentaerythritol  
 triacrylate, tetrabromobisphenol A diacrylate, triglycerol  
 diacrylate, trimethylolpropane triacrylate,  
 tris(acryloxyethyl) isocyanurate, ethylene glycol  
 dimethacrylate, diethylene glycol dimethacrylate,  
 triethylene glycol dimethacrylate, tetraethylene glycol  
 dimethacrylate, polyethylene glycol dimethacrylate,  
 propylene glycol dimethacrylate, polypropylene glycol  
 dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-  
 butanediol dimethacrylate, 1,6-hexanediol dimethacrylate,  
 neopentyl glycol dimethacrylate, 2-hydroxy-1,3-  
 dimethacryloxypropane, 2,2-bis[4-  
 (methacryloxy)phenyl]propane, 2,2-bis[4-  
 (methacryloxyethoxy)-phenyl]propane, 2,2-bis[4-  
 (methacryloxyethoxy diethoxy)-phenyl]propane, 2,2-bis[4-  
 (methacryloxyethoxy polyethoxy)-phenyl]propane,  
 tetrabromobisphenol A dimethacrylate, dicyclopentany  
 dimethacrylate, dipentaerythritol hexamethacrylate,  
 glycerol dimethacrylate, hydroxyl pivalic acid neopentyl  
 glycol dimethacrylate, dipentaerythritol monohydroxy  
 pentamethacrylate, ditrimethylolpropane tetramethacrylate,  
 pentaerythritol trimethacrylate, pentaerythritol  
 tetramethacrylate, triglycerol dimethacrylate, trimethylol  
 propane trimethacrylate, tris(methacryloxyethyl)iso-

cyanurate, allyl methacrylate, divinylbenzene, diallyl phthalate, diallyl terephthalate, diallyl isophthalate and diethylene glycol bisallylcarbonate.

[0108]

The microencapsulated pigment of the invention having the crosslinked structure has a long-term excellent storage stability in the aqueous medium including various aqueous organic solvents and water and has a long-term excellent storage stability in the aqueous medium including a compound selected from the group consisting of glycol ethers and 1,2-alkylene glycol-based surfactants or a compound selected from the group consisting of acetylene glycol-based surfactants and acetylene alcohol-based surfactants. Although the reason for this is not clear, it is conceivable as one reason for this that the solvent resistance is improved due to the polymer having the crosslinked structure.

The added amount of the cross-linking monomer is preferably within the range of 0.0001 to 0.05 time the molarity of the above-mentioned hydrophobic monomer, and more preferably in the range of 0.001 to 0.01 time the molarity thereof. Exceeding 0.05 time the molarity of the hydrophobic monomer unfavorably results in the occurrence of a deterioration in fixability or abrasion resistance, and an increase in particle size in some cases. It is



preferred that the amount of the above-mentioned crosslinking monomer added is appropriately decided within the above-mentioned range, considering the solvent resistance, fixability and abrasion resistance.

[0109]

The polymerization of the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group, a copolymerization of the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group and the cationic polymerizable surfactant, and the copolymerization of the hydrophobic monomer and the crosslinking monomer can be started preferably by adding a polymerization initiator thereto, and particularly, a water-soluble polymerization initiator is preferably used as the polymerization initiator. Examples of the polymerizable initiator can include potassium persulfate, ammonium persulfate, sodium persulfate, 2,2-azobis-(2-methylpropionamidine) dihydrochloride and 4,4-azobis-(4-cyano-valeric acid).

[0110]

A preferable method of preparing a microencapsulated pigment according to the first embodiment of the invention can include adding the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group (the hydrophobic monomer and the crosslinking monomer may

be further added thereto) and water as needed to the aqueous dispersion of the pigment particles, dispersing the pigment particles by irradiating ultrasonic waves thereto, raising the temperature up to a predetermined temperature (a temperature at which the polymerization initiator is activated) while performing the irradiation of ultrasonic waves and the stirring, adding the polymerization initiator thereto, and performing emulsion polymerization by activating the polymerization initiator.

A preferable method of preparing a microencapsulated pigment according to the second embodiment of the invention can include adding the cationic polymerizable surfactant to the aqueous dispersion of the pigment particles having an anionic group on the surface thereof, adding water or water and an aqueous medium thereto as needed, irradiating ultrasonic waves thereto for a predetermined time, then adding the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group (the hydrophobic monomer and the crosslinking monomer may be further added thereto) and water as needed thereto, dispersing the pigment particles by irradiating ultrasonic waves thereto again for a predetermined time, raising the temperature up to a predetermined temperature (a temperature at which the polymerization initiator is activated) while performing

the irradiation of ultrasonic waves and the stirring, adding the polymerization initiator thereto, and performing emulsion polymerization by activating the polymerization initiator.

When the hydrophobic monomer is used, more specifically, the cationic polymerizable surfactant having a cationic group, a hydrophobic group, and a polymerizable group to the aqueous dispersion of the pigment particles having an anionic group on the surfaces thereof, ultrasonic waves are irradiated thereto, then the hydrophobic monomer is mixed thereinto, the anionic polymerizable surfactant having an anionic group, a hydrophobic group, and a polymerizable group and/or the hydrophilic monomer having an anionic group are mixed thereto, ultrasonic waves are irradiated thereto, and the polymerization initiator is added thereto again, thereby performing the emulsion polymerization.

[0111]

In preparing the microencapsulated pigment, the polymerization reaction such as the emulsion polymerization or the mini-emulsion polymerization is performed using a reaction vessel equipped with a ultrasonic generator, a stirrer, a reflux condenser, a dropping funnel, and a temperature controller.

The activation of the polymerization initiator can

be properly performed by raising the temperature of the aqueous dispersion up to a predetermined polymerization temperature. After the polymerization is ended, the resultant dispersion is preferably filtered within the range of PH 7.0 to 9.0. Here, the aqueous medium is a solvent containing water as a major component as described above and may contain an aqueous medium such as glycerin or glycol as components other than water. The polymerization temperature is preferably in the range of 60°C to 90°C. when the pigment particles having an anionic group as the hydrophilic group on the surfaces thereof is not in the aqueous dispersion state, the dispersion process is performed preferably using a general dispersion instrument such as a ball mill, a roll mill, an Eiger mill, and a jet mill as pretreatment.

[0112]

In the microencapsulate pigment according to the invention obtained as described above, it is conceivable that the pigment particles having a small average particle size are completely encapsulated with the polymer layer (without defects), and that the hydrophilic groups of the polymer layer are regularly orientated toward the aqueous medium (see Figs. 2, 4, and 6). Accordingly, the pigment has high dispersion stability to the aqueous medium.

The particle size of the microencapsulated pigment

is preferably 400 nm or less, more preferably 300 nm or less, and particularly preferably from 50 to 200 nm.

[0113]

The above-mentioned microencapsulated pigment can be obtained as an aqueous dispersion in which the microencapsulated pigment is dispersed in an aqueous medium. The aqueous medium in which the microencapsulated pigment is dispersed may contain unreacted materials derived from the used monomers other than the microencapsulated pigment, that is, unreacted materials derived from (a) the cationic polymerizable surfactant, (b) the hydrophobic monomer, and (c) the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group.

The ink for ink jet recording according to the invention is obtained by purifying the aqueous dispersion in which the microencapsulated pigment is dispersed and properly adding an additive to the aqueous dispersion as needed. According to the invention, by purifying the aqueous dispersion and reducing the concentration of the unreacted materials derived from the components of the coating polymer of the microencapsulated pigment, the print density of a printed image is enhanced, thereby obtaining the ink for ink jet recording which can prevent the blurring when plain paper is used as the recording

medium and has an excellent glossy property when glossy paper is used.

[0114]

The concentration of the unreacted (c) anionic polymerizable surfactant and/or hydrophilic monomer having an anionic group after the purification is preferably 50000 ppm or less and more preferably 10000 ppm or less, based on a water component.

Here, the "water component" means that it is obtained by removing insoluble components such as the microencapsulated pigment from the aqueous dispersion and includes, for example, unreacted polymerizable surfactants and unreacted monomers.

The "unreacted (c) anionic polymerizable surfactant and/or hydrophilic monomer having an anionic group" means that it does not contribute to the formation of the coating polymer of the microencapsulated pigment among (c) the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group and includes polymers or oligomers formed by polymerizing the anionic polymerizable surfactant and/or the hydrophilic monomer, in addition to the polymerizable surfactant as a monomer and/or the hydrophilic monomer. It is considered that the unreacted hydrophilic monomer is soluble by the unreacted polymerizable surfactant.

[0115]

When the microencapsulated pigment according to the invention is formed by adding (a) the cationic polymerizable surfactant and (c) the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group to the aqueous dispersion in which the pigment particles are dispersed and polymerizing the resultant solution, the total concentration of the unreacted (a) and (c) after purifying the aqueous dispersion containing the microencapsulated pigment is preferably 50000 ppm or less and more preferably 10000 ppm or less, based on the water components in the aqueous dispersion.

When the microencapsulated pigment is formed by adding (b) the hydrophobic monomer thereto in addition to the polymerizable surfactant and performing the polymerization, the total concentration of the unreacted (a), (b), and (c) after the purification is preferably 50000 ppm or less and more preferably 10000 ppm or less, based on the water components in the aqueous dispersion.

[0116]

Among the components of the coating polymers of the microencapsulated pigment, particularly, (c) the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group is excessively added so as to

stabilize the encapsulated particles before the polymerization as described above. Accordingly, the concentration of the unreacted (c) after the polymerization tends to increase and thus it is estimated that the above-mentioned effect can become more remarkable by controlling the concentration of the unreacted (c) in the aqueous dispersion.

In the concentrations of the unreacted materials before performing the purification, it is preferable that the concentration of (a) is in the range of 5 to 40% by weight, the concentration of (b) is in the range of 5 to 40% by weight, and the concentration of (c) is in the range of 5 to 40% by weight.

[0117]

As a method for purifying the aqueous dispersion containing the microencapsulated pigment, there can be used centrifugal separation, ultrafiltration, or the like.

In the invention, the concentrations of (a), (b), and (c) contained in the aqueous dispersion can be measured by the following first method or second method.

[0118]

(First Method)

That is, the spectral characteristics of the cationic polymerizable surfactant, the anionic polymerizable surfactant, and the hydrophilic monomer



having an anionic group dissolved in ion exchanged water are previously measured with a spectrophotometer, and a calibration curve is determined from the amount of each material dissolved in ion exchanged water and the absorbance at a characteristic absorption wavelength. Then, the resulting aqueous dispersion of the microencapsulated pigment is centrifuged at 20,000 revolutions for 30 minutes with a centrifugal separator, and the resulting supernatant is diluted to a specified dilution (for example, a 100-fold dilution). The absorbance of this diluted solution at 200 to 400 nm was measured with a spectrophotometer, and the amount of each material in the supernatant is determined from the above-mentioned calibration curve.

[0119]

Further, as to the hydrophobic monomer, the spectral characteristics of the hydrophobic monomer dissolved in an organic solvent such as n-hexane is previously measured with a spectrophotometer to determine a calibration curve from the amount dissolved in the organic solvent such as n-hexane and the absorbance at a characteristic absorption wavelength. Then, the resulting aqueous dispersion of the microencapsulated pigment is mixed with the organic solvent such as n-hexane, and an organic solvent phase is collected and diluted to a specified dilution. The

absorbance of this diluted solution at 200 to 400 nm was measured with a spectrophotometer, and the amount of the hydrophobic monomer extracted in the organic solvent such as n-hexane is determined from the above-mentioned calibration curve.

[0120]

(Second Method)

The cationic polymerizable surfactant, the anionic polymerizable surfactant, and the hydrophilic monomer dissolved in ion exchanged water are previously subjected to liquid chromatography, and a calibration curve is determined from the amount of each material dissolved in the ion exchanged water and the retention time. Then, the resulting dispersion of the microencapsulated pigment is centrifuged at 20,000 revolutions for 30 minutes with a centrifugal separator, and the resulting supernatant is separated by liquid chromatography. The amounts of the cationic polymerizable surfactant, the anionic polymerizable surfactant, and the hydrophilic monomer in the supernatant are determined from the retention amounts of the cationic polymerizable surfactant, the anionic polymerizable surfactant, and the hydrophilic monomer at each retention time, and the above-mentioned calibration curve.

[0121]

As for the hydrophobic monomer, the hydrophobic monomer dissolved in the organic solvent such as tetrahydrofuran is previously subjected to liquid chromatography to determine a calibration curve from the amount dissolved in the organic solvent such as tetrahydrofuran and the retention time. Then, the resulting aqueous dispersion of the microencapsulated pigment is mixed with the organic solvent such as tetrahydrofuran. An organic solvent phase is collected and separated by liquid chromatography. The amount of the hydrophobic monomer extracted in the organic solvent such as tetrahydrofuran is determined from the retention amount of the hydrophobic monomer at retention time, and the above-mentioned calibration curve.

[0122]

By adding other mixed components for preparing the ink for ink jet recording to the aqueous dispersion purified as described above by the use of a general method, the ink for ink jet recording according to the embodiments of the invention can be manufactured.

[0123]

The ink for ink jet recording according to the embodiments of the invention includes the aqueous dispersion containing the microencapsulated pigment and can be prepared by properly adding an additive such as an

aqueous medium, a viscosity adjuster, and an antimold usually used in the ink for ink jet recording.

The content of the microencapsulated pigment is preferably in the range of 1 to 20% by weight and more preferably in the range of 3 to 15% by weight, based on the total weight of the ink for ink jet recording. The content is preferably in the range of 5 to 15% by weight so as to obtain high print density and high color developability.

The solvent of the ink for ink jet recording according to the embodiments of the invention preferably contains water and a water-soluble organic solvent as basic solvents and may further contain another component as needed.

[0124]

Examples of the water-soluble organic solvents can include alkyl alcohols having 1 to 4 carbon atoms such as ethanol, methanol, butanol, propanol, and isopropanol, glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-propyl ether, diethylene glycol mono-iso-propyl ether, ethylene glycol mono-n-butyl ether,

diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-t-butyl ether, 1-methyl-1-methoxy butanol, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-iso-propyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-iso-propyl ether, propylene glycol mono-n-butyl ether, and dipropylene glycol mono-n-butyl ether, formamide, acetamide, dimethyl sulfoxide, sorbite, sorbitan, acentine, diacetine, triacetine, and sulforan.

[0125]

In order to impart water retentivity and wetting properties to the ink for ink jet recording, the ink for ink jet recording according to the embodiment of the invention preferably contains a wetting agent comprising a high boiling-point water-soluble organic solvent as a water-soluble organic solvent. Such a high boiling-point water-soluble organic solvent is a high boiling-point water-soluble organic solvent having a boiling point of 180°C or higher.

[0126]

Specific examples of the water-soluble organic

solvents having a boiling point of 180°C or higher, which can be used in the invention, include ethylene glycol, propylene glycol, diethylene glycol, pentamethylene glycol, trimethylene glycol, 2-butene-1,4-diol, 2-ethyl-1,3-hexanediol, 2-methyl-2,4-pentanediol, tripropylene glycol monomethyl ether, dipropylene glycol monoethyl glycol, tetraethylene glycol, triethylene glycol, tripropylene glycol, polyethylene glycol having a molecular weight of 2,000 or less, 1,3-propylene glycol, isopropylene glycol, isobutylene glycol, glycerol, meso-erythritol and pentaerythritol. It is more preferred that the high boiling water-soluble organic solvent used in the invention has a boiling point of 200°C or higher. One or two or more of them can be used in the ink of the invention. Addition of the high boiling water-soluble organic solvent to the ink can provide the ink for ink jet recording which retains flowability and re-dispersibility for a long period of time even when it is allowed to stand in an open state (a state in which the ink is in contact with air at room temperature). Further, such an ink is hard to clog ink jet nozzles during printing using an ink jet printer or on restarting after the interruption of printing, so that the ink having high ejection stability from the ink jet nozzles is obtained.

[0127]

The total content of the water-soluble organic solvent is preferably in the range of 10 to 50% by weight, and more preferably in the range of 10 to 30% by weight, based on the total weight of the ink for ink jet recording.

[0128]

Examples of the water-soluble organic solvent can include 2-pyrrolidone, N-methylpyrrolidone,  $\epsilon$ -caprolactam, dimethyl sulfoxide, sulforane, morpholine, N-ethylmorpholine and 1,3-dimethyl-2-imidazolidinone can be added to the ink and one or more thereof may be selected and used. Addition of the polar solvent can provide the effect of improving the dispersibility of the encapsulated pigment particles in the ink to improve the ejection stability of the ink.

The content of the polar solvent is preferably in the range of 0.1 to 20% by weight and more preferably in the range of 1 to 10% by weight, based on the total weight of the ink for ink jet recording.

[0129]

In order to accelerate penetration of the aqueous medium into the recording medium, it is preferred that the ink for ink jet recording according to an embodiment of the invention further contains a penetrant. Prompt penetration of the aqueous medium into the recording medium can provide recorded matter having images with less

blurring. As such penetrants, there are preferably used an alkyl ether of a polyhydric alcohol (also referred to as a glycol ether) and a 1,2-alkyldiol. The alkyl ethers of polyhydric alcohols include, for example, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-i-propyl ether, diethylene glycol mono-i-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-t-butyl ether, 1-methyl-1-methoxybutanol, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-i-propyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-i-propyl ether, propylene glycol mono-n-butyl ether and dipropylene glycol mono-n-butyl ether. The 1,2-alkyldiols include, for example, 1,2-pentanediol and 1,2-hexanediol. Besides, the penetrants may selected from diols of straight-chain hydrocarbons such as 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-



hexanediol, 1,7-heptanediol and 1,8-octanediol.

[0130]

In particular, in an embodiment of the invention, it is preferred that at least one selected from propylene glycol monobutyl ether, dipropylene glycol monobutyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, 1,2-pentanediol and 1,2-hexanediol is used as the penetrant. The total content of these penetrants is preferably from 1 to 20% by weight, and more preferably from 1 to 10% by weight, based on the total weight of the ink for ink jet recording. When the content of the penetrant is adjusted to 1% by weight or more, the effect of improving the penetrability of the ink into the recording medium is obtained. Further, adjustment to 20% by weight or less can prevent the occurrence of blurring in images printed using this ink, and can prevent an excessive increase in the viscosity of the ink. In particular, when the 1,2-alkyldiol such as 1,2-pentanediol or 1,2-hexanediol is used in the ink, drying properties of the ink after printing are improved, and blurring in images can be decreased.

[0131]

Particularly, in the embodiments of the invention, by allowing the ink to contain glycerine, it is possible to sufficiently secure clogging reliability and storage

stability of the ink.

By allowing the ink to contain one or more selected from the group consisting of alkyl ether and 1,2-alkyl diol of polydydric, it is possible to enhance penetrability of the ink solvent component into the recording medium. Accordingly, in view of the effect of the microencapsulated pigment according to the embodiment of the invention, it is possible to greatly reduce the blurring of an image in the process of performing a printing operation on the plain paper or a recycled paper and to enhance the print quality.

[0132]

When the above-mentioned glycol ethers are used, it is particularly preferable that glycol ethers are used along with an acetylene glycol compound as a surfactant to be described later.

[0133]

Furthermore, it is preferred that the ink for ink jet recording according to an embodiment of the invention contains a surfactant, particularly an anionic surfactant and/or a nonionic surfactant. Specific examples of the anionic surfactants include an alkanesulfonate, an  $\alpha$ -olefinsulfonate, an alkylbenzenesulfonate, an alkylnaphthalenesulfonic acid, an acylmethyltaurinic acid, a dialkylsulfosuccinic acid, an alkylsulfuric ester salt,

a sulfated oil, a sulfated olefin, a polyoxyethylene alkyl ether sulfuric ester salt, a fatty acid salt, an alkylsarcosine salt, an alkylphosphoric ester salt, a polyoxyethylene alkyl ether phosphoric ester salt and a monoglyceride phosphoric ester salt. Further, specific examples of the nonionic surfactants include a polyoxyethylene alkyl ether, a polyoxyethylene alkyl phenyl ether, a polyoxyethylene alkyl ester, a polyoxyethylene alkylamide, a glycerol alkyl ester, a sorbitan alkyl ester, a sugar alkyl ester, a polyhydric alcohol alkyl ether and an alkanolamine fatty acid amide.

[0134]

More specifically, the anionic surfactants include ether surfactants such as sodium dodecylbenzenesulfonate, sodium laurate and an ammonium salt of a polyoxyethylene alkyl ether sulfate. Specific examples of the nonionic surfactants include polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene dodecyl phenyl ether, a polyoxyethylene alkyl allyl ether, polyoxyethylene oleyl ether, polyoxyethylene lauryl ether, a polyoxyethylene alkyl ether and a polyoxyalkylene alkyl ether, and ester surfactants such as polyoxyethylene oleic acid, polyoxyethylene oleic acid ester, polyoxyethylene distearic acid ester, sorbitan laurate, sorbitan monostearate, sorbitan monooleate, sorbitan sesquioleate,

polyoxyethylene monooleate and polyoxyethylene stearate.

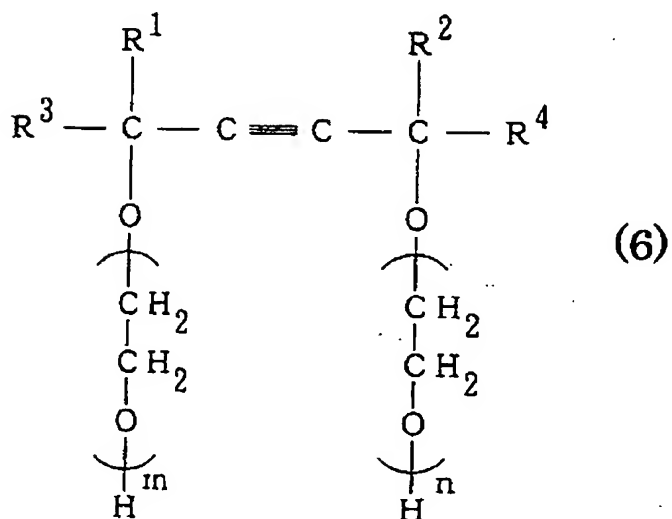
[0135]

In particular, it is desirable that the ink for ink jet recording according to an embodiment of the invention contains an acetylene glycol-based surfactant and/or an acetylene alcohol-based surfactant. The aqueous medium contained in the ink becomes easy to penetrate into the recording medium thereby, so that images having little blurring can be printed on various recording media.

Preferred specific examples of the acetylene glycol-based surfactants used in the invention include a compound represented by the following formula (6).

[0136]

[Kagaku 11]



[0137]

In formula (6), m and n are each a number satisfying  $0 \leq m+n \leq 50$ ; and  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are each independently an alkyl group (preferably, an alkyl group having 6 or less carbon atoms).

Of the compounds represented by the above formula (6), particularly preferred are 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 3,6-dimethyl-4-octyne-3,6-diol and 3,5-dimethyl-1-hexyne-3-ol. As the compounds represented by the above formula (6), it is also possible to utilize commercial products commercially available as the acetylene glycol-based surfactants. Specific examples thereof include Surfynol 104, 82, 465, 485 and TG (all are available from Air Products and Chemicals, Inc.), and Olfine STG and Olfine E1010 (trade names, manufactured by Nissin Chemical Industry Co., Ltd.).

[0138]

The acetylene alcohol-based surfactants include Surfynol 61 (available from Air Products and Chemicals, Inc.).

[0139]

The content of the surfactant is in the range of 0.01 to 10% by weight and more preferably in the range of 0.1 to 5% by weight, based on the total weight of the ink for ink jet recording.

[0140]

Further, the ink for ink jet recording according to the embodiment of the invention can contain a pH adjuster. The pH of the ink is adjusted preferably to 7 to 9, and more preferably to 7.5 to 8.5.

Preferred specific examples of the pH adjusters include potassium metal compounds such as sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, sodium hydrogencarbonate, potassium carbonate, lithium carbonate, sodium phosphate, potassium phosphate, lithium phosphate, potassium dihydrogenphosphate, dipotassium hydrogenphosphate, sodium oxalate, potassium oxalate, lithium oxalate, sodium borate, sodium tetraborate, potassium hydrogenphthalate and potassium hydrogentartrate; ammonia; and amines such as methyl amine, ethylamine, diethylamine, trimethylamine, triethyl amine, tris(hydroxymethyl)aminomethane hydrochloride, triethanolamine, diethanolamine, diethylethanolamine, triisopropenol amine, butyldiethanolamine, morpholine and propanol amine.

Of these, when an alkali hydroxide compound or an amine alcohol added to the ink, the dispersion stability of the microencapsulated pigment particles of the invention in the ink can be improved.

The added amount of the alkali hydroxide compound is preferably in the range of 0.01 to 5% by weight, and more

preferably in the range of 0.05 to 3% by weight, based on the total weight of the ink.

The added amount of the amine alcohol is preferably in the range of 0.1 to 10% by weight, and more preferably in the range of 0.5 to 5% by weight, based on the total weight of the ink.

[0141]

Further, for the purpose of mildewproofing, antiseptis or rust prevention, at least one compound selected from benzoic acid, dichlorophene, hexachlorophene, sorbic acid, a p-hydroxybenzoic ester, ethylenediamine tetraacetic acid (EDTA), sodium dehydroacetate, 1,2-benthiazolin-3-on (product name: Proxel XL manufactured by Avecia) and 4,4-dimethyloxazolidine can be added to the ink for ink jet recording.

Furthermore, for the purpose of preventing nozzles of a recording head from being dried, at least one selected from the group consisting of urea, thiourea and ethylene urea can also be added to the ink for ink jet recording.

[0142]

A particularly preferred embodiment of the ink for ink jet recording of the invention is an ink containing at least

(1) the above-mentioned microencapsulated pigment,

(2) at least one compound (penetrant) selected from the group consisting of diethylene glycol monobutyl ether, triethylene glycol monobutyl ether and an 1,2-alkyldiol having 4 to 10 carbon atoms,

(3) glycerol; and

(4) water.

Such an ink for ink jet recording particularly has excellent dispersion stability and ejection stability and does not have the clogging of the nozzles for a long period of time, thereby stably performing a printing operation. In the recording medium such as the plain paper, the recycled paper, and the coated paper, the drying property after the printing operation is excellent and the blurring is little, thereby obtaining a high-quality image with a high print density and excellent color developability.

[0143]

Another particularly preferred embodiment of the ink for ink jet recording of the invention contains at least

(1) the microencapsulated pigment according to the embodiment of the invention,

(2) at least one compound (penetrant) selected from the group consisting of diethylene glycol monobutyl ether, triethylene glycol monobutyl ether and an 1,2-alkyldiol having 4 to 10 carbon atoms,



(3) the acetylene glycol-based surfactant and/or the acetylene alcohol-based surfactant,

(4) glycerol, and

(5) water.

Such an ink for ink jet recording particularly has excellent dispersion stability and ejection stability and does not have the clogging of the nozzles for a long period of time, thereby stably performing a printing operation. In the recording medium such as the plain paper, the recycled paper, and the coated paper, the drying property after the printing operation is excellent and the blurring is little, thereby obtaining a high-quality image with a high print density and excellent color developability.

[0144]

In general, the dispersant such as a surfactant or a polymer dispersant is used to disperse the pigment. Since the dispersants are simply adsorbed on the surfaces of the pigment particles, the dispersants tends to be separated from the surfaces of the pigment particles due to some environmental reasons. On the contrary, in the embodiment of the invention, since the polymer coating or the crosslinking polymer coating surrounding the surfaces of the pigment surfaces completely including the surfaces of the pigment particles having a hydrophilic group with the

polymer coating or the crosslinking polymer coating is secured very strongly to the surfaces of the pigment particles as described above, the dispersant is hardly separated from the surfaces of the pigment particles.

[0145]

More specifically, in the ink of which the penetrability has been improved with the acetylene glycol-based surfactant and/or an acetylene alcohol-based surfactant, and a penetrant such as diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, propylene glycol monobutyl ether, dipropylene glycol monobutyl ether, and 1,2-alkyl diol by the use of the pigment dispersion in which the pigment is dispersed using a surfactant or a dispersant such as a polymer dispersant, the dispersant is easily separated from the surfaces of the pigment particles due to the strong shearing force applied when the ink is ejected through a thin nozzle, thereby deteriorating the dispersibility and making the ejection unstable.

[0146]

On the contrary, in the ink for ink jet recording using the microencapsulated pigment according to the embodiment of the invention, such a phenomenon is not recognized to eject the ink stably. Since the pigment particles are encapsulated with the polymer coating or the

crosslinking polymer coating to obtain excellent solvent resistance, the promotion of the separation from the pigment particles or the expansion of the polymer due to the penetrant hardly occurs, thereby maintaining the excellent dispersion stability for a long period of time.

[0147]

In the ink composition employing the pigment dispersion in which the pigment is dispersed using the dispersant such as the surfactants or the polymer dispersants and having improved penetrability, since the viscosity of the ink composition tends to increase due to the dispersant not adsorbed on the surfaces of the pigment particles but dissolved in the solution at the initial time of dispersion or there is a tendency that the dispersant is separated from the pigment particles after being dispersed and the viscosity of the ink composition increases due to the separated dispersant. Accordingly, in the plain paper or the recycled paper, a sufficient print density cannot be obtained and thus excellent color developability cannot be often obtained. On the contrary, in the ink composition using the microencapsulated pigment according to the embodiment of the invention, since the pigment particles are encapsulated with the polymer coating or the crosslinking polymer coating as described above, the dispersant is not easily separated from the

pigment particles and thus the viscosity of the ink composition does not increase. Accordingly, it is easy to decrease the viscosity of the ink composition and it is possible to more contain the pigment particles, thereby obtaining a sufficient print density on the plain paper or the recycled paper.

[0148]

In the particularly preferable embodiment of the invention, the added amount of diethylene glycol monobutyl ether and triethylene glycol monobutyl ether as the penetrant of (2) is preferably 10% by weight or less, and more preferably in the range of 0.5 to 5% by weight, based on the total weight of the ink. Addition of diethylene glycol monobutyl ether and triethylene glycol monobutyl ether can remarkably improve penetrability of the ink, thereby enhancing the print quality. Further, the addition of diethylene glycol monobutyl ether and/or triethylene glycol monobutyl ether also improves the solubility of the acetylene glycol-based surfactant.

[0149]

In the particularly preferable embodiment of the invention, the amount added at the time when the 1,2-alkyldiol having 4 to 10 carbon atoms of (2) as the penetrant is added to the ink is 15% by weight or less based on the total weight of the ink. When the 1,2-

alkyldiol having 3 or less carbon atoms is used, sufficient penetrability into the recording medium is not obtained. The 1,2-alkyldiol having 16 or more carbon atoms is unfavorable because it becomes difficult to dissolve in water. When the amount of the 1,2-alkyldiol in the ink exceeds 15% by weight, the viscosity of the ink unfavorably tends to increase. Specifically, 1,2-pentanediol or 1,2-hexanediol is preferably used as the 1,2-alkyldiol. The added amount of the 1,2-pentane diol is preferably in the range of 3 to 15% by weight. Good penetrability cannot be obtained when it is less than 3% by weight. The added amount of 1,2-hexandiol is preferably in the range of 0.5 to 10% by weight. When the added amount of 1,2-Hexanediol is smaller than 0.5 % by, good penetrability cannot be obtained.

[0150]

Further, when the ink for ink jet recording according to the embodiment described above contains preferably a solid wetting agent in the range of 0.5 to 20% by weight based on the total weight of the ink, in order to make it difficult to generate the clogging of the ink jet nozzles (improvement in clogging reliability).

The above-mentioned solid wetting agent means a water-soluble substance which is solid at the ordinary temperature (25°C) and has a water-retaining function.

Preferred examples of the solid wetting agents include a saccharide, a sugar alcohol, a hyaluronate, trimethylolpropane and 1,2,6-hexanetriol. Examples of the saccharides include a monosaccharide, a disaccharide, an oligosaccharide (including a trisaccharide and a tetrasaccharide) and a polysaccharide. Preferred examples thereof include glucose, mannose, fructose, ribose, xylose, arabinose, galactose, aldonic acid, glucitol, sorbit, maltose, cellobiose, lactose, sucrose, trehalose and maltotriose. The term "polysaccharide" as used herein means a saccharide in its broad sense, and is used in the sense that it includes substances widely occurring in nature such as alginic acid,  $\alpha$ -cyclodextrin and cellulose. Further, derivatives of these saccharides include a reduced sugar of the above-mentioned saccharide (for example, a sugar alcohol represented by the general formula  $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$  (wherein  $n$  represents an integer of 2 to 5), an oxidized sugar (for example, an aldonic acid or a uronic acid), an amino acid and a thiosugar. In particular, a sugar alcohol is preferred, and specific examples thereof include maltitol, sorbitol and xylitol. As the hyaluronate, there can be used a product commercially available as a 1% aqueous solution of sodium hyaluronate (molecular weight: 350,000). The solid wetting agents may be used alone or as a mixture of two or

more. Trimethylol propane and 1,2,6-hexatriol are particularly preferably used as the solid wetting agent.

[0151]

The use of the solid wetting agent can restrain the evaporation of water by its water retaining function, so that the viscosity of the ink does not increase in flow paths of the ink or in the vicinities of ink jet nozzles, and the film formation caused by the evaporation of water of the ink also becomes difficult to occur, which causes difficulty in clogging the nozzles. Further, the above-mentioned solid wetting agent is chemically stable, so that it does not decompose in the ink, and the quality of the ink can be maintained for a long period of time. Furthermore, even when the above-mentioned solid wetting agent is added to the ink, the ink does not wet a nozzle plate, and can be stably ejected from the ink jet nozzles. Such ability is excellent particularly when trimethylol propane and 1,2,6-hexane triol are used.

[0152]

In the invention, when the above-mentioned solid wetting agents are used alone, the content thereof is preferably from 0.5 to 20% by weight, and more preferably from 3 to 10% by weight, based on the total weight of the ink. When two or more thereof are used as a mixture, the total amount of two or more thereof is preferably in the

range of 0.5 to 20% by weight and more preferably in the range of 3 to 10% by weight, based on the total weight of the ink for ink jet recording. When two or more thereof are used as a mixture, preferred is a combination of one selected from the group consisting of a saccharide, a sugar alcohol and a hyaluronate and one selected from the group consisting of trimethylolpropane and 1,2,6-hexanetriol. This combination is preferred because an increase in the viscosity of the ink by addition can be restrained. When the content of the solid wetting agents is less than 3% by weight, the sufficient effect of improving the clogging is not obtained. On the other hand, exceeding 20% by weight results in the tendency of the harmful effect to occur that the viscosity increases to become hard to obtain stable ejection.

[0153]

In the particularly preferable embodiment of the invention, the added amount of (3) the acetylene glycol-based surfactant and/or the acetylene alcohol-based surfactant is preferably in the range of 0.01 to 10% by weight and more preferably in the range of 0.1 to 5% by weight, based on the total weight of the ink.

[0154]

Although the ink for ink jet recording according to the embodiments of the invention has been described above,



the microencapsulated pigment according to the embodiments of the invention contained as the colorant has a shape of true sphere as described above. Accordingly, flowability of the ink easily becomes Newtonian and the anionic groups on the surface are regularly densely orientated toward the aqueous medium, so that electrostatic repulsion is considered to be effectively generated. There can be therefore prepared the ink for ink jet recording which is excellent in ejection stability, more excellent in dispersibility (high dispersibility) and dispersion stability and further improved in the concentration of the colorant contained, compared to the conventional microencapsulated pigments.

[0155]

In the ink for ink jet recording according to the invention, the concentration of the unreacted materials derived from the components of the coating polymers of the microencapsulated pigment, that is, the concentration of (c) the anionic polymerizable surfactant and/or the hydrophilic monomer having an anionic group, decreases in the aqueous dispersion after forming the microencapsulated pigment. Accordingly, it is possible to obtain an ink for ink jet recording which can further enhance the print density of a printed image, prevent the blurring of an image when plain paper is used as the recording medium,

and have an excellent glossy property when glossy paper is used.

[0156]

The ink jet recording can be suitably achieved by mounting the ink for ink jet recording according to the embodiment of the invention on a known ink jet printer, and printing the ink on the recording medium such as plain paper or an ink jet recording medium. This allows ejection stability of the ink from a recording head to be excellent, and can provide the recorded matter which is excellent in fastness, abrasion resistance, and color developability of images, and high in image density of images, and in which images are hard to blur. Further, even when plain paper is used as the recording medium, the recorded matter is obtained in which images are hard to blur, and which is excellent in color developability of images.

[Examples]

[0157]

Hereinafter, the invention will be more specifically described with reference to examples and comparative examples, but the invention is not limited to the examples.

[0158]

The "amount of hydrophilic groups onto the surfaces of the pigment particles" in the following description was

obtained as follows.

"Introduced Amount of Anionic Groups"

(When anionic groups were introduced using a sulfonating agent)

Pigment particles whose surfaces are treated with a sulfonating agent were treated by an oxygen flask combustion method, and a 0.3% aqueous solution of hydrogen peroxide was absorbed by the pigment particles. Then, the sulfuric ion (bivalent) was determined by ion chromatography (Dionex Corporation; 2000i). The resulting value was converted to the value of the sulfonic acid group, and indicated as the equivalent per g of pigment (mmol/g).

(When anionic groups were introduced using a carboxylating agent)

As a technique, the Zeisel method was used. Diazomethane was dissolved in an appropriate solvent, and the resulting solution was added dropwise to convert all active hydrogen atoms on the surfaces of the pigment particles to methyl groups. Hydroiodic acid having a specific gravity of 1.7 was added to the pigment thus treated, followed by heating to vaporize the methyl groups as methyl iodide. The gas of methyl iodide was trapped with a silver nitrate solution to precipitate as methylsilver iodide. The amount of the original methyl

groups, that is, the amount of active hydrogens, was measured from the weight of the silver iodide, and indicated as the molar quantity per g of pigment (mmol/g). that is, the amount of active hydrogen on the surfaces of the pigment particles corresponds to the amount of carboxyl acid groups.

[0159]

#### Preparation of Cyan Pigment Particles "P3" Having Anionic Groups on Their Surfaces

A phthalocyanine pigment (C.I. Pigment Blue 15:3) (20 parts) was mixed with 500 parts of quinoline, and dispersed in an Eiger Motor Mill, M250 (manufactured by Eiger Japan Co., Ltd.) under the conditions of a bead loading of 70% and 5,000 revolutions for 2 hours. A mixed solution of a pigment paste dispersed and a solvent was transferred to an evaporator, and heated at 120°C while reducing the pressure to 30 mmHg or lower, thereby removing water contained in the system by distillation as much as possible. Thereafter, the temperature was controlled to 150°C, and then, 20 parts of a sulfonated pyridine complex (a sulfonating agent) was added, and allowed to react for 8 hours. After the termination of the reaction, the reaction product was washed several times with excess quinoline, poured into water, and filtered, thereby obtaining cyan pigment particles "P3"

having hydrophilic groups (anionic groups) on their surfaces.

The amount of the anionic groups introduced into the resulting cyan pigment particles "P3" was 0.04 mmol/g.

[0160]

Preparation of Magenta Pigment Particles "P5" Having Hydrophilic Groups (Anionic Groups) on Their Surfaces

Magenta pigment particles "P5" having the hydrophilic groups on their surfaces were obtained by the same treating method as in the above-mentioned "preparation of cyan pigment particles "P3" having the hydrophilic groups on their surfaces", except that "20 parts of the phthalocyanine pigment (C.I. Pigment Blue 15:3)" was substituted by "20 parts of an isoindolinone pigment (C.I. Pigment Red 122)."

The amount of the hydrophilic groups (anionic groups) introduced into the resulting yellow pigment particles "P5" was 0.06 mmol/g.

[0161]

Preparation of Microencapsulated Pigment Dispersions "MCP1" and "MCP2"

Preparation of Microencapsulated Pigment Dispersion "MCP1"

1.0 g of dimethylaminoethylmethyl chloride methacrylate as the cationic polymerizable surfactant was

added to an aqueous dispersion in which 100 g of cyan pigment particles having anionic groups on the surfaces thereof were dispersed in 500 g of ion exchange water and then ultrasonic waves were irradiated to the mixture for 15 minutes. Subsequently, 7.0 g of Aqualon KH-5 as the anionic polymerizable surfactant, 2.0 g of 2-acrylamide-2-methylpropane sulfonate, and 50 g of ion exchange water were added and mixed thereto, and then ultrasonic waves were irradiated thereto for 30 minutes.

This was put into a reaction vessel equipped with a stirrer, a reflux condenser, a dropping funnel, a temperature controller, a nitrogen-introducing pipe, and an ultrasonic generator. Then, after the internal temperature of the reaction vessel was elevated to 80°C, an potassium persulfate solution with 0.3 g of potassium persulfate dissolved therein as a polymerization initiator was added dropwise and polymerization was conducted at 80°C for 6 hours, while introducing nitrogen into the reaction vessel. After the termination of the polymerization, pH was adjusted to 8 with 2 mmol/l of potassium hydroxide and the resultant solution was filtered with a membrane filter having a hole diameter of 1  $\mu\text{m}$  to remove the large particles, thereby obtaining the desired dispersion "MCP1" including the microencapsulated pigment.

[0162]

A part of the obtained microencapsulated pigment dispersion "MCP1" was centrifuged at 2000 revolutions for 30 minutes with a centrifugal separator. Then, the obtained supernatant was diluted to 100 times and absorbance thereof at 200 to 400 nm was measured with a spectrophotometer. Then, the amounts of dimethylaminoethylmethyl chloride methacrylate, Aqualon KH-5, and 2-acrylamide-2-methylpropane sulfonate in the supernatant were calculated and to obtain the unreacted amount by the use of the calibration curve previously acquired at a specific wavelength of dimethylaminoethylmethyl chloride methacrylate, Aqualon KH-5, and 2-acrylamide-2-methylpropane sulfonate. In the concentration of the unreacted materials, the concentration of dimethylaminoethylmethyl chloride methacrylate was 10 wt%, the concentration of 2-acrylamide-2-methylpropane sulfonate was 10 wt%, and the concentration of Aqualon KH-5 was 40 wt%.

On the other hand, the obtained microencapsulated pigment dispersion "MCP1" was filtered with an ultrafiltering instrument by the use of a cross flow method. A part of the dispersion after the ultrafiltration was subjected to the same processes as described above and the amount of the unreacted materials

was obtained from the dissolved amounts of dimethylaminoethylmethyl chloride methacrylate, Aqualon KH-5, and 2-acrylamide-2-methylpropane sulfonate in the supernatant. The concentrations of the unreacted materials, that is, dimethylaminoethylmethyl chloride methacrylate, 2-acrylamide-2-methylpropane sulfonate, and Aqualon KH-5, were all less than 10000 ppm.

[0163]

#### Preparation of Microencapsulated Pigment Dispersion "MCP2"

2.0 g of dimethylaminoethylmethyl chloride methacrylate as the cationic polymerizable surfactant was added to an aqueous dispersion in which 100 g of magenta pigment particles having anionic groups on the surfaces thereof were dispersed in 500 g of ion exchange water and then ultrasonic waves were irradiated to the mixture for 15 minutes. Subsequently, 12 g of benzyl methacrylate, 8.0 g of dodecyl methacrylate, 4.0 g of Aqualon KH-10 as the anionic polymerizable surfactant, 2.0 g of 2-acrylamide-2-methylpropane sulfonate, and 50 g of ion exchange water were added and mixed thereto, and then ultrasonic waves were irradiated thereto for 30 minutes.

This was put into a reaction vessel equipped with a stirrer, a reflux condenser, a dropping funnel, a temperature controller, a nitrogen-introducing pipe, and



an ultrasonic generator. Then, after the internal temperature of the reaction vessel was elevated to 80°C, a potassium persulfate solution with 0.6 g of potassium persulfate dissolved therein as a polymerization initiator was added dropwise in 20 g of the ion exchange water and polymerization was conducted at 80°C for 6 hours while introducing nitrogen into the reaction vessel. After the termination of the polymerization, pH was adjusted to 8 with 2 mmol/l of potassium hydroxide and the resultant solution was filtered with a membrane filter having a hole diameter of 1  $\mu$ m to remove the large particles, thereby obtaining the desired dispersion "MCP2" including the microencapsulated pigment.

[0164]

A part of the obtained microencapsulated pigment dispersion "MCP2" was centrifuged at 2000 revolutions for 30 minutes with a centrifugal separator. Then, the obtained supernatant was diluted to 100 times and absorbance thereof at 200 to 400 nm was measured with a spectrophotometer. Then, the amounts of dimethylaminoethylmethyl chloride methacrylate, Aqualon KH-10, and 2-acrylamide-2-methylpropane sulfonate in the supernatant were calculated and to obtain the unreacted amount by the use of the calibration curve previously acquired at a specific wavelength of

dimethylaminoethylmethyl chloride methacrylate, Aqualon KH-10, and 2-acrylamide-2-methylpropane sulfonate. In the concentration of the unreacted materials, the concentration of dimethylaminoethylmethyl chloride methacrylate was 10 wt%, the concentration of 2-acrylamide-2-methylpropane sulfonate was 10 wt%, and the concentration of Aqualon KH-10 was 40 wt%.

A part of the microencapsulated pigment dispersion "MCP2" was mixed with n-hexane, an organic solvent was taken therefrom, and absorbance thereof at 200 to 400 nm was measured with a spectrophotometer. Then, the dissolved amounts of benzyl methacrylate and dodecyl methacrylate in the taken n-hexane solution were calculated to acquire the unreacted amounts thereof by the use of the calibration serves previously obtained at specific wavelengths of benzyl methacrylate and dodecyl methacrylate. In the concentrations of the unreacted materials, the concentration of benzyl methacrylate was 10 wt% and the concentration of dodecyl methacrylate was 10 wt%.

[0165]

On the other hand, the obtained microencapsulated pigment dispersion "MCP2" was filtered with an ultrafiltering instrument by the use of a cross flow method. A part of the dispersion after the

ultrafiltration was subjected to the same processes as described above and the unreacted amount A was obtained from the dissolved amounts of dimethylaminoethylmethacrylate, Aqualon KH-10, and 2-acrylamide-2-methylpropane sulfonate in the supernatant. A part of the dispersion after the ultrafiltering was mixed with n-hexane, an organic solvent was taken therefrom, and absorbance thereof at 200 to 400 nm was measured with a spectrophotometer. Then, the unreacted amount B was calculated from the dissolved amounts of benzyl methacrylate and dodecyl methacrylate in the taken n-hexane solution by the use of the calibration curves previously obtained at specific wavelengths of benzyl methacrylate and dodecyl methacrylate. The total amount of the unreacted amount A and the unreacted amount B was less than 10000 ppm.

[0166]

[Kagaku 12]

[0167]

As a result of measuring an aspect ratio and a Zingg index of the microencapsulated pigment dispersions "MCP1" and "MCP2", the aspect ratio was 1.0 and the Zingg index

was 1.0, thereby showing a true sphere shape. The aspect ratio and the Zingg index were determined by diluting the aqueous dispersion 100 times with ion exchange water, drying it, and observing the particles under a transmission electron microscope (TEM) and a scanning electron microscope (SEM) to measure the major and minor diameters and thickness of the particles.

[0168]

#### Preparation of Ink for Ink Jet Recording

The inks for ink jet recording according to Examples 1 and 2 were prepared using the purified microencapsulated pigment dispersions "MCP1" and "MCP2" on the basis of the compositions shown in Table 1. In Comparative Examples 1 and 2, the inks for ink jet recording were prepared using the microencapsulated pigment dispersions "MCP1" and "MCP2" before the purification.

[0169]

[Table 1]

		Ex. 1	Ex. 2	Com. Ex. 1	Com. Ex. 4
Microencapsulated Pigment	MCP1 (Purified)	8			
	MCP2 (Purified)		8		
	MCP1 (Not Purified)			8	
	MCP2 (Not Purified)				8
Wetting Agent	Glycerol	12	13	12	13
Penetrant	Diethylene glycol monobutyl ether		3		
	Triethylene glycol monobutyl ether	4		4	2
Solid Wetting Agent	Trimethylolpropane	3	2	3	2
	1,2,8-Hexanetriol		1		1
Polar Solvent	2-Pyrrolidone		1		1
Surfactant	Olfine E1010	1	1	1	1
pH Adjuster	Potassium hydroxide	0.1	0.1	0.1	0.1
Preservative	Proxel XL-2	0.05	0.05	0.05	0.05
Water	Ion exchanged water	bal.	bal.	bal.	bal.

[0170]

The inks for ink jet recording according to Examples 1 and 2, and Comparative Examples 1 and 2 and the recorded matters printed using the inks were evaluated as follows.

[0171]

#### Evaluation 1: Glossiness

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PX-V700C (manufactured by Seiko Epson Corporation). A solid print was made on a 50mm×50mm region of PM Photographic Paper at a duty of 100%. Then, the glossiness was evaluated with naked eyes.

A: The ink has a high gloss.

B: The ink has a gloss.

C: The ink has a poor gloss.

[0172]

#### Evaluation 2: Glossiness Stain

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PM-720C (manufactured by Seiko Epson Corporation). A gray-scale image was printed on PM Photographic Paper (manufactured by Seiko Epson Corporation).

A: A gloss difference is not recognized between the gray-scale images.

B: A gloss difference is not felt between the gray-scale images.

C: A gloss difference is recognized between the gray-scale images.

[0173]

#### Evaluation 3: Color Developability

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PX-V700C (manufactured by Seiko Epson Corporation). A solid print was made on each of PM photographic paper (manufactured by Seiko Epson Corporation) and Xerox P paper (manufactured by Xerox Corp.), and the C\* value of the solid print portion was

measured. The color developability was evaluated according to the following criteria:

AA: 85 or more;

A: 80 or more

B: 70 to less than 80;

C: 50 to less than 70; and

D: less than 50.

[0174]

#### Evaluation 4: Abrasion Resistance

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PX-V700C (manufactured by Seiko Epson Corporation). A solid print was made in a 10mm×10mm region on PM photographic paper (glossy) manufactured by Seiko Epson Corporation at a duty of 100%. After standing at a temperature of 25°C for 1 hour, the above-mentioned printed region was rubbed with a yellow highlight pen using an aqueous ink (ZEBRA PEN2 (trademark) manufactured by Zebra Pen Corporation) at a load of 500 g and at a speed of 10 mm/sec, and it was observed whether a stain occurred or not. The results thereof were evaluated according to the following criteria:

AA: No stain occurs at all when the printed region was rubbed triple

A: No stain occurs at all when the printed region

was rubbed twice.

B: No stain occurs when the printed region was rubbed once, but a stain occurs when it was rubbed twice.

C: A stain occurs when the printed region was rubbed once.

[0175]

#### Evaluation 5: Water Resistance

An ink cartridge was filled with each of the inks for ink jet recording of Examples and Comparative Examples, and mounted on an ink jet printer, PX-V700C (manufactured by Seiko Epson Corporation). 24 alphabet characters were printed on Xerox P paper (manufactured by Xerox Corp.) and was left at 25°C for 1 hour and 1 ml of ion exchange water was dropped on the print region. The state after 20 minutes was visually observed, and evaluated according to the following criteria.

A: No change occurs on all papers.

B: A colorant slightly bleeds out of the printed portion, but the recognition of letters is possible.

C: A colorant bleeds out of the printed portion to make the contours of printed letters unclear, so that the recognition of the letters is difficult.

[0176]

#### Evaluation 6: Ejection Stability

Each of the inks for ink jet recording of Examples



and Comparative Examples was mounted on an ink jet printer, PX-700C (manufactured by Seiko Epson Corporation), and 1-mm ruled lines were printed on super fine paper designed for ink jet printing manufactured by Seiko Epson Corporation. The state of printing such as dot missing and deviation in ink landing position was visually observed, and evaluated according to the following criteria.

AA: Even when 20,000 or more prints are carried out, neither dot missing nor deviation from the ink landing position occurs.

A: Even when 10,000 or more prints are carried out, neither dot missing nor deviation from the ink landing position occurs.

B: When 1,000 to less than 10,000 prints are carried out, dot missing or deviation from the ink landing position occurs.

C: When 100 to less than 1,000 prints are carried out, dot missing or deviation from the ink landing position occurs.

D: When less than 100 prints are carried out, dot missing or deviation from the ink landing position occurs.

[0177]

#### Evaluation 7: Clogging Reliability

After the printing conducted in the above-mentioned

evaluation 6, a power supply of the printer was turned off, and the ink was allowed to stand. After one week, the same printing test was conducted. The "state of ink ejection" at that time was visually observed, and evaluated according to the following criteria.

A: Normal printing starts without a cleaning operation at the same time that print signals are transmitted to the printer.

B: Normal printing is conducted after three or less cleaning operations.

C: Normal printing is conducted after six or less cleaning operations.

D: Normal printing cannot be conducted even when a cleaning operation is repeated seven or more times.

[0178]

[Table 2]

	Example 1	Example 2	Comparative Example 1	Comparative Example 1
Evaluation 1	A	A	C	C
Evaluation 2	A	A	C	C
Evaluation 3	AA	AA	A	A
Evaluation 4	B	AA	B	AA
Evaluation 5	A	A	A	A
Evaluation 6	AA	AA	A	A
Evaluation 7	A	A	A	A

[0179]

As shown in Table 2, it can be seen that the glossiness and the glossiness stain are poor in Comparative Examples 1 and 2 not subjected to the purification, but are excellent in Examples 1 and 2 subjected to the purification. It can be also seen that Examples 1 and 2 are excellent in color developability and ejection stability.

[Brief Description of the Drawings]

[0180]

[Fig. 1] Fig. 1 is a schematic view showing a state in which pigment particles are dispersed in an aqueous medium and coexist with an anionic polymerizable surfactant.

[Fig. 2] Fig. 2 is a schematic view showing a state in

which the anionic polymerizable surfactant is polymerized in the dispersed state shown in Fig. 1.

[Fig. 3] Fig. 3 is a schematic view showing a state where pigment particles having an anionic group on the surfaces thereof are dispersed in the aqueous medium and coexist with a cationic polymerizable surfactant and an anionic polymerizable surfactant.

[Fig. 4] Fig. 4 is a schematic view showing a state where the cationic polymerizable surfactant and the anionic polymerizable surfactant are polymerized in the dispersed state shown in Fig. 3.

[Fig. 5] Fig. 5 is a schematic view showing a state where pigment particles having an anionic group on the surfaces thereof are dispersed in the aqueous medium and coexist with a cationic polymerizable surfactant and an anionic polymerizable surfactant.

[Fig. 6] Fig. 6 is a schematic view showing a state where the cationic polymerizable surfactant and the anionic polymerizable surfactant are polymerized in the dispersed states shown in Fig. 5.

[Description of Reference Numerals and Signs]

[0181]

1, 21: PIGMENT PARTICLE

2: CATIONIC POLYMERIZABLE SURFACTANT

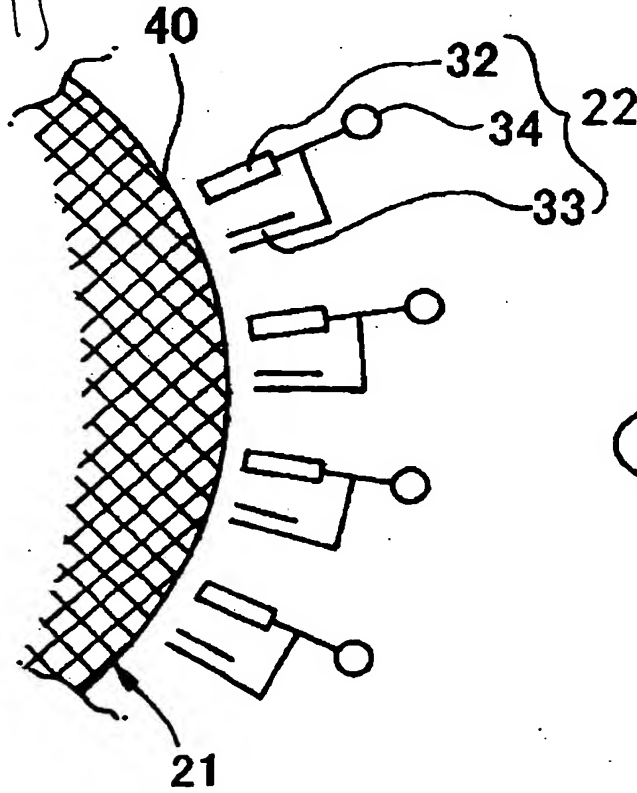
3, 22: ANIONIC POLYMERIZABLE SURFACTANT

10: HYDROPHILIC GROUP  
11: CATIONIC GROUP  
12, 12', 32: HYDROPHOBIC GROUP  
13, 13', 33: POLYMERIZABLE GROUP  
14, 14', 34: ANIONIC GROUP  
60, 60', 41: POLYMER LAYER (POLYMER)  
100, 100', 110: MICROENCAPSULATED PIGMENT

~~【書類名】 図面~~  
~~【図1】~~

[Designation of Document] Drawings

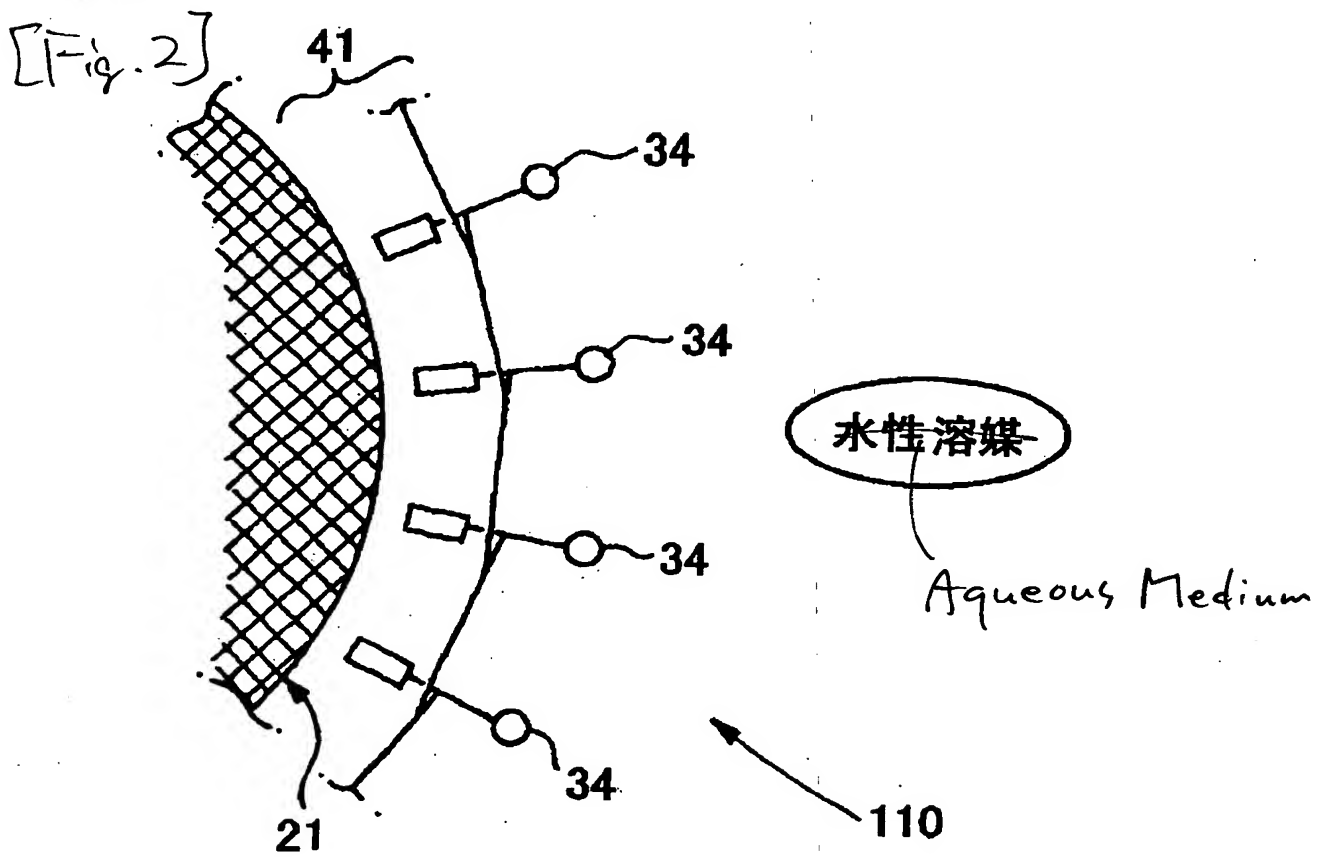
[Fig. 1]



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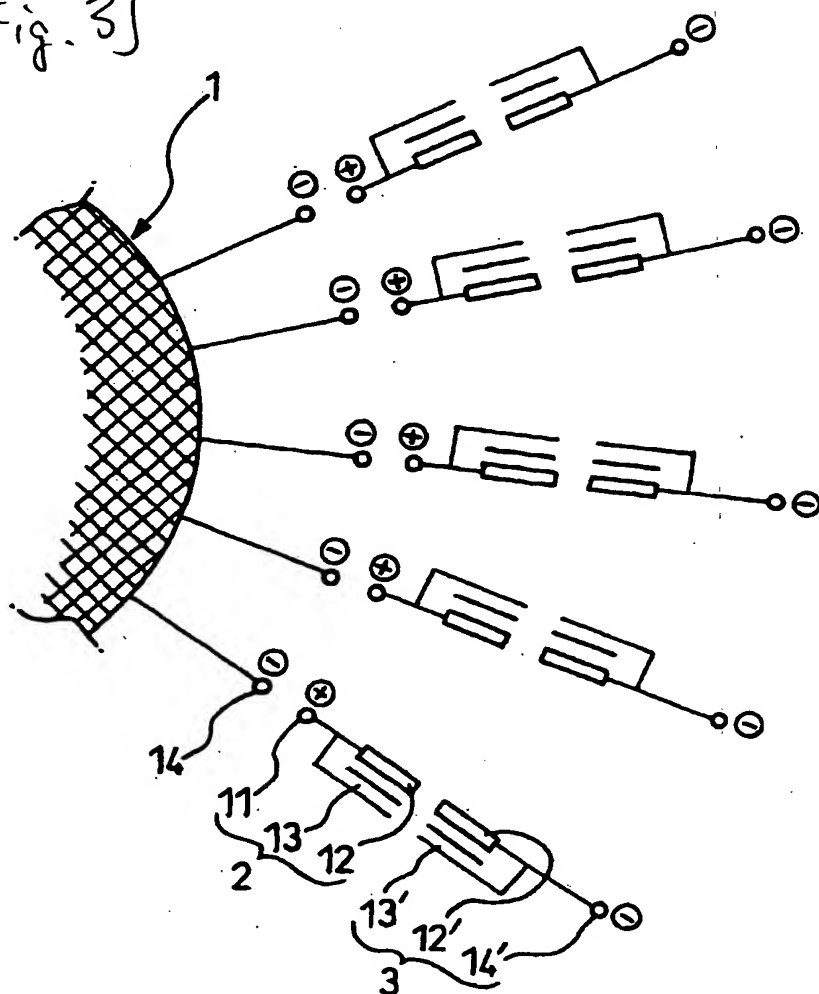
Aqueous Medium

【図2】



【図3】

{Fig. 3}

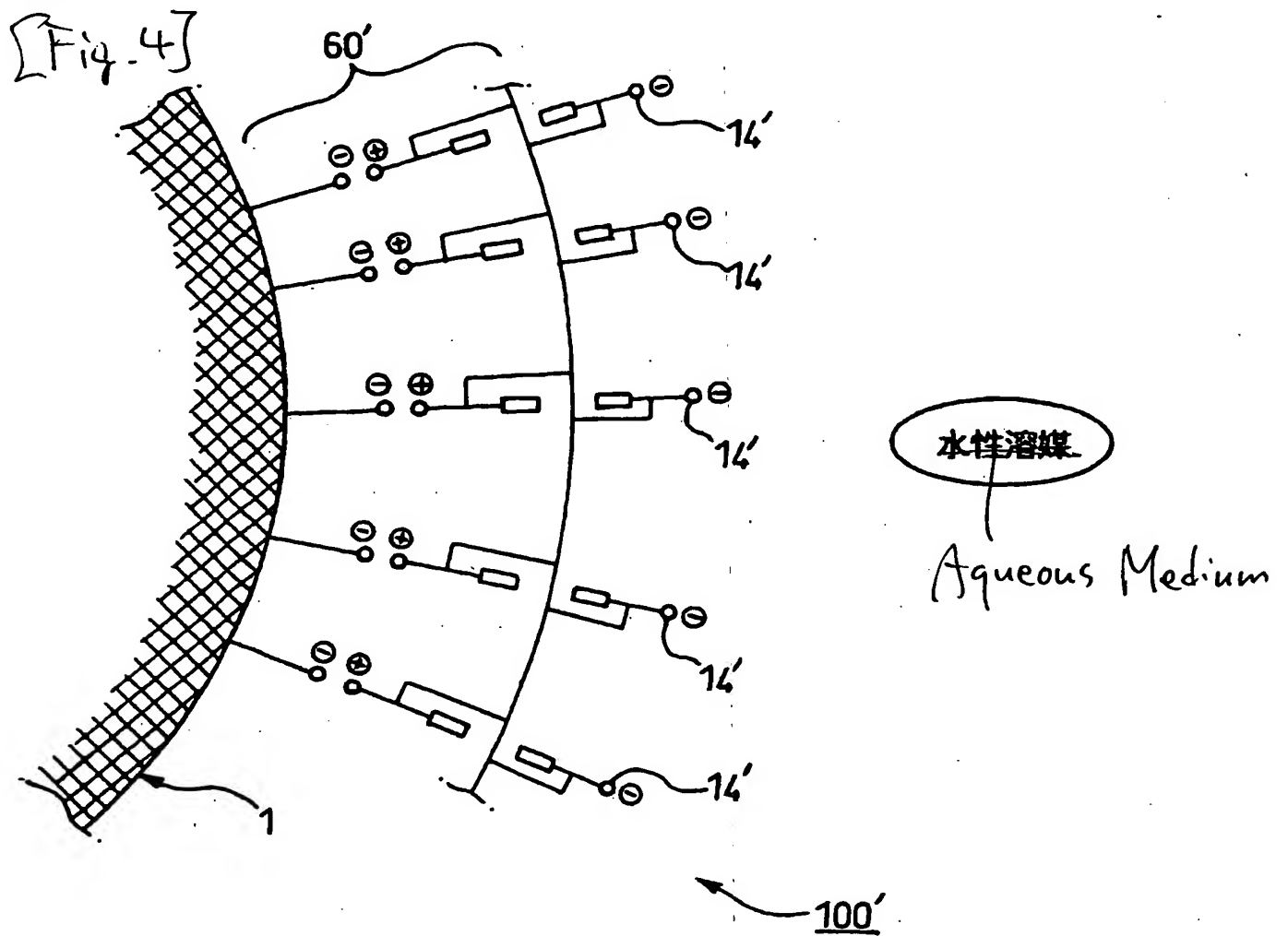


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Aqueous Medium

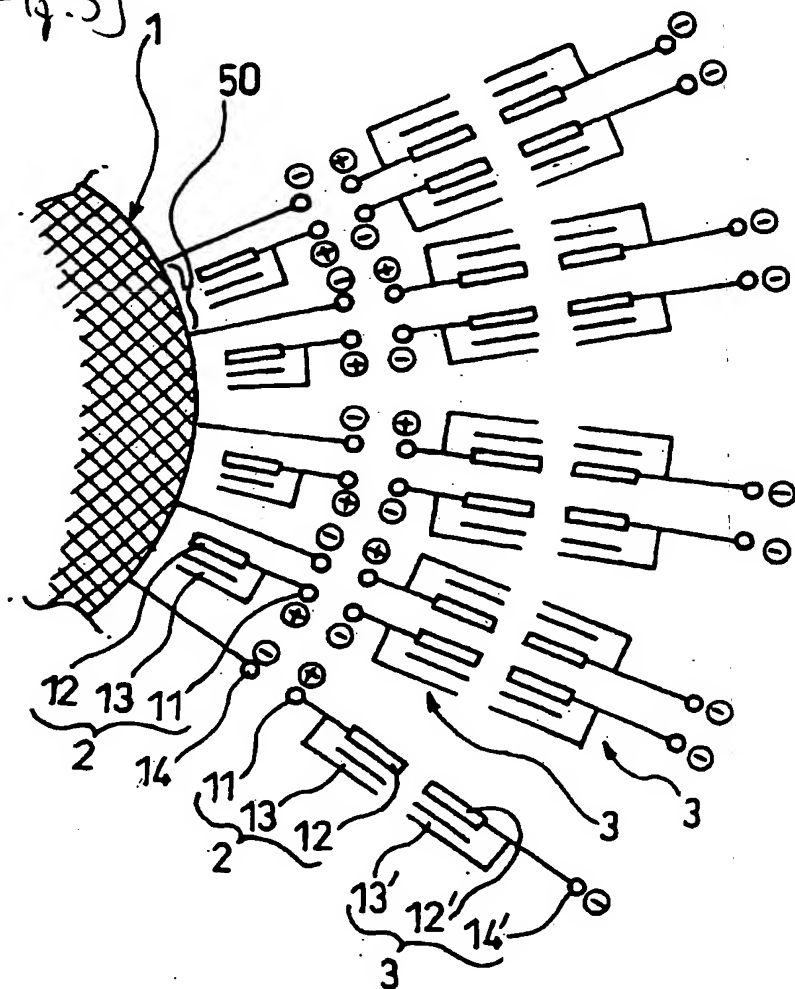


【図4】



【図5】

[Fig. 5]

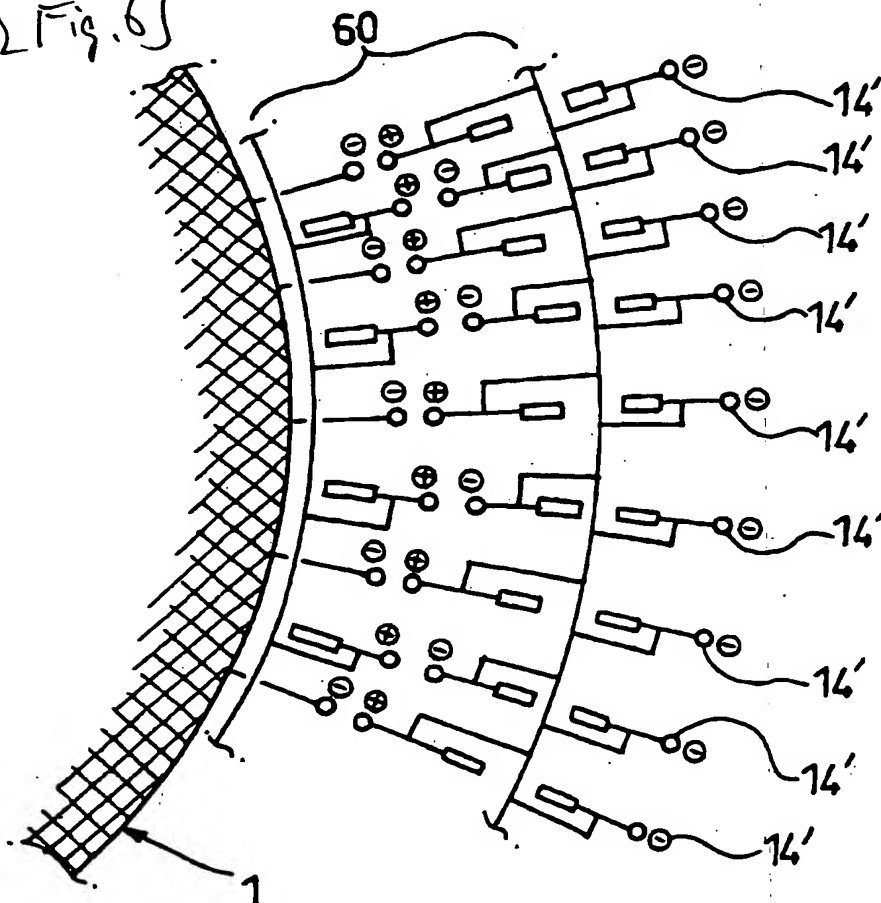


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Aqueous Medium

【図6】

[Fig. 6]



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Aqueous Medium

[Designation of Document] ABSTRACT

[Abstract]

[Task] To provide an ink for ink jet recording in which a print density of a recorded image is high, blurring hardly occurs when plain paper is used as a recording medium, and a glossy property is excellent when glossy paper is used.

[Means for Resolution] Provided is an ink for ink jet recording containing an aqueous dispersion of a microencapsulated pigment which is formed by adding (c) an anionic polymerizable surfactant and/or a hydrophilic monomer having an anionic group to an aqueous dispersion in which pigment particles are dispersed and polymerizing the added aqueous dispersion, the ink for ink jet recording being prepared by purifying the aqueous dispersion of the microencapsulated pigment, wherein the concentration of unreacted (c) after the purification treatment is 50000 ppm or less based on the aqueous component in the aqueous dispersion.

[Selected Drawing] None